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ELECTRONIC SUPPLEMENTARY INFORMATION

Reactions of Dicobalt Octacarbonyl with Dinucleating and Mononucleating Bis(imino)pyridine Ligands

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1. General Experimental Details

All reactions involving air-sensitive materials were carried out in a nitrogen-filled glovebox. 2,7-Di-*tert*-butyl-9,9-dimethyl-4,5-diaminoxanthene was synthesized using previously published procedures.[1] Cobalt carbonyl, ethyl propiolate, and 2,4,6-trimethylaniline were purchased from Sigma and used as received. 2,6-Pyridinedicarboxaldehyde was purchased from TCI and used as received. All non-deuterated solvents were purchased from Aldrich and were of HPLC grade. The non-deuterated solvents were purified using an MBraun solvent purification system. Acetonitrile-d_3, benzene-d_6, dichloromethane-d_2, and toluene-d_8 were purchased from Cambridge Isotope Laboratories. All solvents were stored over 3 Å molecular sieves. Compounds were generally characterized by ^{1}H and ^{13}C NMR, high-resolution mass spectrometry and/or elemental analysis, IR spectroscopy, and UV-Vis spectroscopy. Selected compounds were characterized by X-ray crystallography. NMR spectra of the ligands and metal complexes were recorded at the Lumigen Instrument Centre (Wayne State University) on an Agilent DD2-600 MHz Spectrometer, a Varian VNMRS-500 MHz Spectrometer or an Agilent 400 MHz Spectrometer in CD_3CN, C_6D_6, CD_2Cl_2, or C_7D_8 at room temperature. Chemical shifts and coupling constants (J) were reported in parts per million (δ) and Hertz, respectively. High resolution mass spectra of the ligand and metal complexes were collected at the Lumigen Instrument Centre (Wayne State University) on a Thermofisher Scientific LTQ Orbittrap XL mass spectrometer. The MS survey scan was set from 200 – 2000. The resolution was set to 60000. In all cases, only one microscan was used in the analysis. Elemental analysis was performed under ambient air-free conditions by Midwest Microlab LLC. IR spectra of powdered samples were recorded on a Shimadzu IR Affinity-1 FT-IR Spectrometer outfitted with a MIRacle10 attenuated total reflectance accessory with a monolithic diamond crystal stage and pressure clamp. UV-Visible spectra were obtained on a Shimadzu UV-1800 spectrometer. X-ray structures were collected using Bruker Apex2 at the Lumigen Instrument Centre (Wayne State University). Quantitative analysis of arene formation was done by gas chromatography–mass spectrometry using Agilent 6890N spectrometer, Thermo TG5MS 30m × 0.32mm × 0.25μm column, 7683 series injector and Agilent 5973 detector.

2. X-ray Crystallographic Details

Structures of complexes **1'**, **1**, **2**, **3**, and **4** were confirmed by X-ray structure determination. The crystals were mounted on a Bruker APEXII/Kappa three circle goniometer platform diffractometer equipped with an APEX-2 detector. A graphic monochromator was employed for wavelength selection of the Mo Kα radiation (λ = 0.71073 Å). The data were processed and refined using the APEX2 software. Structures were solved by direct methods in SHELXS and refined by standard difference Fourier techniques in the SHELXTL program suite (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using the standard riding model and refined isotropically; all other atoms were refined anisotropically. Crystalline sample of **1** contained both needle-like crystals (**1'**) and plate-like crystals (**1**). The structure of **1'** was of low quality as indicated by its high R factors, and therefore only the overall connectivity and the cobalt-cobalt bonds are discussed. The structure of **4** contained three THF molecules per unit cell; one was found to be severely disordered. Our attempts to model the disorder met with only limited success. The structure of **1** contained one ether molecule per unit cell. Detailed crystal and structure refinement data are given in **Table S1**.

Table S1. X-ray crystallographic details for complexes **1**, **1'**, **2**, **3** and **4**.

complex	**1**×$2C_4H_{10}O$	**1'**×$2C_4H_{10}O$	**2a/2b**	**3**×$3C_4H_8O$	**4**
formula	$C_{78}H_{86}Co_4N_6O_{14}$	$C_{78}H_{86}Co_4N_6O_{14}$	$C_{60}H_{54}Co_4N_6O_{10}$	$C_{66}H_{70}Co_2N_6O_7$	$C_{76}H_{78}Co_4N_{10}O_{10}$
Fw, g/mol	1567.25	1567.24	1254.81	1177.14	1527.26
temperature	100(2)	100(2)	100(2)	100(2)	100(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	*C*2/c	$P2_1/n$	$P2_1$	$P2_1/c$	*P-1*
color	red-purple	red-purple	purple	brown	purple
Z	4	4	2	4	2
a, Å	24.960(3)	20.268(2)	10.3616(10)	19.9171(10)	14.541(6)
b, Å	10.0567(12)	18.2285(17)	11.6941(11)	16.0470(8)	14.765(6)
c, Å	30.999(4)	21.168(2)	23.226(2)	18.9243(9)	20.123(6)
α, deg	90.00	90.00	90.00	90.00	101.991(7)
β, deg	102.7044(15)	90.683(6)	100.813(5)	99.304(3)	90.788(10)
γ, deg	90.00	90.00	90.00	90.00	118.813(5)
V, A^3	7590.6(16)	7820.3(13)	2764.3(4)	5968.8(5)	3670(2)
d_{calcd}, g/cm^3	1.370	1.331	1.508	1.309	1.3819
μ, mm^{-1}	0.926	0.898	1.245	0.614	0.953
2θ, deg	50.70	59.15	48.00	54.48	51.20
$R_1{}^a$ (all data)	0.0740	0.2285	0.0878	0.0934	0.0779
$wR_2{}^b$ (all data)	0.1264	0.3922	0.1019	0.1668	0.1335
$R_1{}^a$ [(I>2σ)]	0.0481	0.1360	0.0491	0.0583	0.0493
$wR_2{}^b$ [(I>2σ)]	0.1096	0.3441	0.0893	0.1454	0.1146
GOF (F^2)	1.014	1.197	1.0342	1.044	1.0188

3. Syntheses and Characterization of L^2 and 1-5

Preparation of L^2

A 25 mL methanol solution of 2,6-pyridinedicarboxaldehyde (0.383 g, 2.84 mmol) and acetic acid (0.1 mL) was added to a 25 mL methanol solution of 2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene-4,5-diamine (1.000 g, 2.84 mmol). The reaction was refluxed overnight, producing a light yellow precipitate that was subsequently collected by filtration. The precipitate was washed with methanol and dried *in vacuo* to afford a light-yellow powder (1.087 g, 1.20 mmol, 85%). ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 8.36 (s, 4H, imino-***H***), 7.97 (d, *J* = 7.7 Hz, 4H, β-***H*** on pyridine), 7.62 (t, *J* = 7.7 Hz, 2H, γ-***H*** on pyridine), 7.30 (d, *J* = 1.8 Hz, 4H, ortho-***H*** on xanthene), 6.92 (d, *J* = 2.2 Hz, 4H, para-***H*** on xanthene), 1.75 (s, 6H, methyl-***H***), 1.69 (s, 6H, methyl-***H***), 1.34 (s, 36H, *tert*-butyl-***H***); ^{13}C{^{1}H} NMR (CD_2Cl_2, 150 MHz) δ 164.29, 154.51, 146.26, 140.48, 139.73, 137.41, 131.52, 122.60, 119.26, 116.83, 35.74, 34.93, 32.08, 31.61, 30.58. HRMS (ESI) Calcd for $[C_{60}H_{66}N_6O_2H]^+$: 903.5325. Found: 903.5391.

Preparation of 1

A 2 mL THF solution of L^2 (45.1 mg, 0.050 mmol) was added to a stirring 2 mL THF solution of $Co_2(CO)_8$ (37.6 mg, 0.110 mmol). The solution color changed from dark-red to red-violet. The reaction was stirred overnight, upon which the volatiles were removed *in vacuo*. The resulting residue was washed with hexane to afford **1** as a red-violet solid (67.9 mg, 0.048 mmol, 96%). X-ray quality crystals were obtained from a concentrated ether solution at -35 °C. ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 8.40 (s, 4H, imino-***H***), 8.11 (br s, 2H, γ-***H*** on pyridine), 7.99 (br s, 4H, β-***H*** on pyridine), 7.50 (d, *J* = 2.2 Hz, 4H, ortho-***H*** on xanthene), 7.36 (d, *J* = 2.2 Hz, 4H, para-***H*** on xanthene), 1.69 (s, 6H, methyl-***H***), 1.62 (s, 6H, methyl-***H***), 1.32 (s, 36H, *tert*-butyl-***H***); ^{13}C{^{1}H} NMR (CD_2Cl_2, 150 MHz) δ 210.75, 203.81, 155.27, 150.09, 146.33, 141.61, 139.91, 131.21, 126.58, 123.89, 121.53, 120.73, 35.70, 35.27, 33.18, 31.53, 30.75. IR (Paratone): ν_{CO} = 2074 cm^{-1}, 2026 cm^{-1}, 1990 cm^{-1}, 1890 cm^{-1}. $\lambda_{max}(\varepsilon_M)$: 719 (6510), 542 (13350), 487 (13010). Anal. Calcd for $C_{70}H_{66}Co_4N_6O_{12}$: C, 59.25; H, 4.69; N, 5.92. Found: C, 58.98; H, 4.90; N, 6.02.

Preparation of 2

A 2 mL THF solution of 1,1'-(pyridine-2,6-diyl)bis(*N*-mesitylmethanimine) (L^1, 37.0 mg, 0.100 mmol) was added to a stirring 2 mL THF solution of $Co_2(CO)_8$ (37.6 mg, 0.110 mmol). The solution color changed from dark-red to purple. The reaction was stirred overnight, upon which the volatiles were removed *in vacuo*. The resulting residue was washed with cold hexane to afford **2** as a purple solid (55.0 mg, 0.088 mmol, 88%). X-ray quality crystals were obtained from a concentrated pentane solution at -35 °C. ^{1}H NMR (C_6D_6, 600 MHz) δ 10.06 (v br s, 2H, imino-***H***), 7.28 (br s, 3H, γ-***H*** and β-***H*** on pyridine), 6.73 (s, 4H, meta-***H*** on mesityl), 2.09 (s, 18H, methyl-***H*** on mesityl); ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz) δ 151.34, 149.73, 149.28, 136.45, 130.60, 129.33, 128.25, 124.99, 122.82, 20.82, 18.48. IR (Paratone): ν_{CO} = 2029 cm^{-1}, 1957 cm^{-1}, 1880 cm^{-1}, 1802 cm^{-1}. $\lambda_{max}(\varepsilon_M)$: 767 (3708), 711 (3672), 556 (5596), 495.5 (5896). Anal. Calcd for $C_{30}H_{27}Co_2N_3O_5$: C, 57.43; H, 4.34; N, 6.70. Found: C, 56.95; H, 4.42; N, 6.54.

Preparation of 3

A 2 mL THF solution of 1,1'-(pyridine-2,6-diyl)bis(*N*-mesitylmethanimine) (L^1, 80.0 mg, 0.217 mmol) was added to a stirring 2 mL THF solution of $Co_2(CO)_8$ (40.0 mg, 0.117 mmol). The solution color changed from dark-red to purple, then gradually to brown. The reaction was stirred overnight, upon which the volatiles were removed *in vacuo*. The resulting residue was washed with several times with hexane. Successive recrystallization from a concentrated ether solution at -35 °C afforded brown X-ray quality crystals of **3** (59.7 mg, 0.062 mmol, 57%). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 21.36, 6.67, 4.63, 1.19. μ_{eff} = 2.4 ± 0.2 μ_B. IR (Paratone): ν_{CO} = 1867 cm^{-1}. $\lambda_{max}(\varepsilon_M)$: 762 (3077), 532.5 (3495), 482(4582).

Preparation of 4 from 1

1 (42.6 mg, 0.030 mmol) was treated with 2 mL of acetonitrile (or CD_3CN), producing a dark-green solution. The reaction was stirred for 30 minutes, upon which the volatiles were removed *in vacuo* to afford **4** as a dark-green solid (45.2 mg, 0.030 mmol, 99%). X-ray quality crystals were obtained from acetonitrile/ether vapor diffusion at -35 °C. ^{1}H NMR (CD_3CN, 600 MHz) δ 9.83 (s, 4H, imino-***H***), 8.75 (t, *J* = 7.8 Hz, 2H, γ-***H*** on pyridine), 7.71 (d, *J* = 7.8 Hz, 4H, β-***H*** on pyridine), 7.63 (d, *J* = 1.8 Hz, 4H, ortho-***H*** on xanthene), 7.60 (d, *J* = 1.8 Hz, 4H, para-***H*** on xanthene), 1.96 (s, 12H, acetonitrile-***H***), 1.92 (s, 6H, methyl-***H***), 1.62 (s, 6H, methyl-***H***), 1.34

(s, 36H, *tert*-butyl-***H***); $^{13}C\{^{1}H\}$ NMR (CD_3CN, 150 MHz) δ 157.63, 150.94, 147.49, 142.97, 141.30, 133.05, 128.66, 122.39, 121.09, 119.47, 36.68, 35.46, 34.38, 31.78, 26.85. IR (Paratone): ν_{CO} = 1868 cm^{-1}. $\lambda_{max}(\varepsilon_M)$: 857.5 (2549), 676.5 (1828), 438.5 (7067).

Preparation of 5 from 2

2 (31.4 mg, 0.050 mmol) was treated with 2 mL of acetonitrile (or CD_3CN), producing a dark-green solution. The reaction was stirred for 30 minutes, upon which the volatiles were removed *in vacuo* to afford **5** as a dark-green solid (33.8 mg, 0.030 mmol, 99%). ^{1}H NMR (CD_3CN, 600 MHz) δ 9.73 (s, 2H, imino-***H***), 8.81 (t, *J* = 6.4 Hz, 1H, γ-***H*** on pyridine), 7.95 (d, *J* = 7.0 Hz, 2H, β-***H*** on pyridine), 6.98 (s, 4H, meta-***H*** on mesityl), 2.30 (s, 6H, para-methyl-***H*** on mesityl), 1.94 (s, 12H, ortho-methyl-***H*** on mesityl); $^{13}C\{^{1}H\}$ NMR (CD_3CN, 150 MHz) δ 157.92, 152.21, 151.19, 136.73, 129.99, 129.75, 128.28, 122.49, 21.03, 18.25. IR (Paratone): ν_{CO} = 1868 cm^{-1}. $\lambda_{max}(\varepsilon_M)$: 855 (2176), 630.5 (1104), 443.5 (6680).

4. NMR Spectra

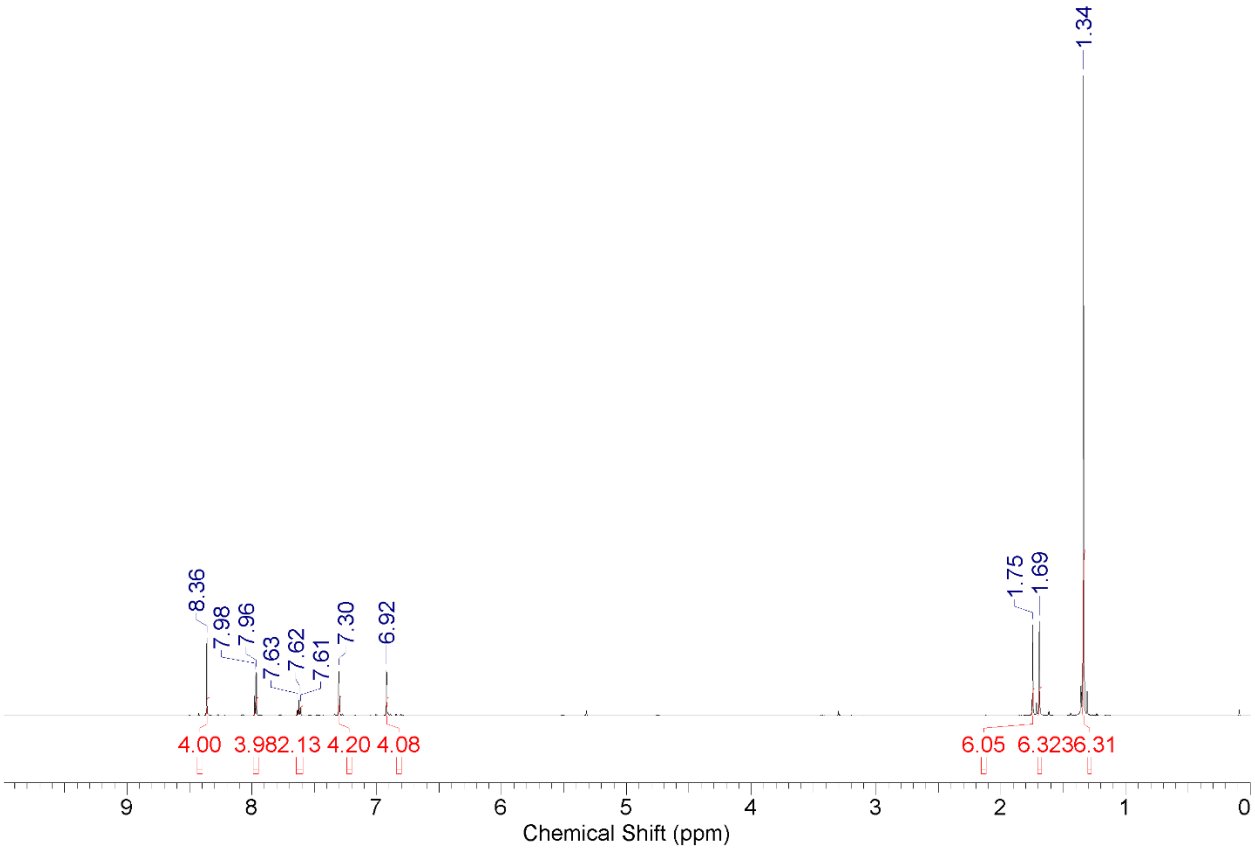

Figure S1: ^{1}H spectrum of **L^{2}** (CD_2Cl_2, 600 MHz).

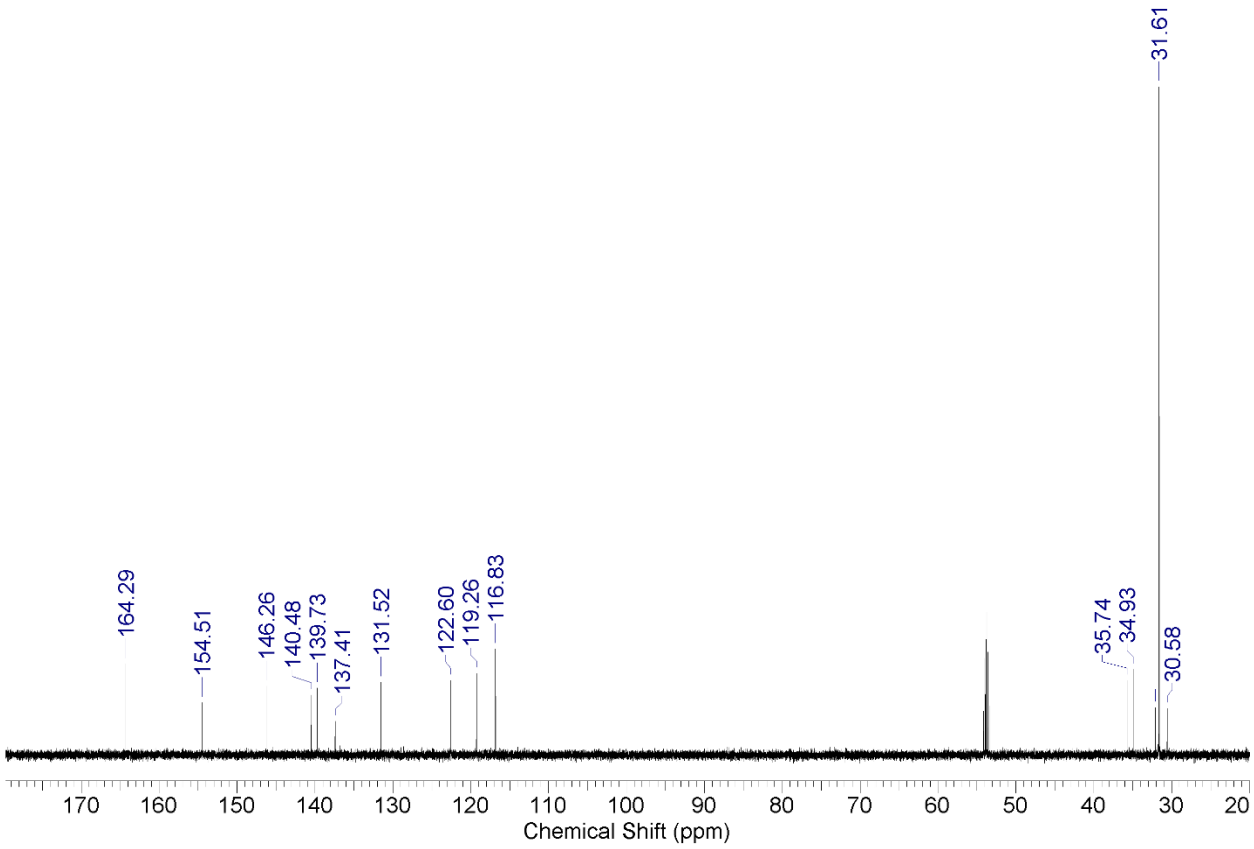

Figure S2: ^{13}C spectrum of $\mathbf{L^2}$ (CD_2Cl_2, 150 MHz).

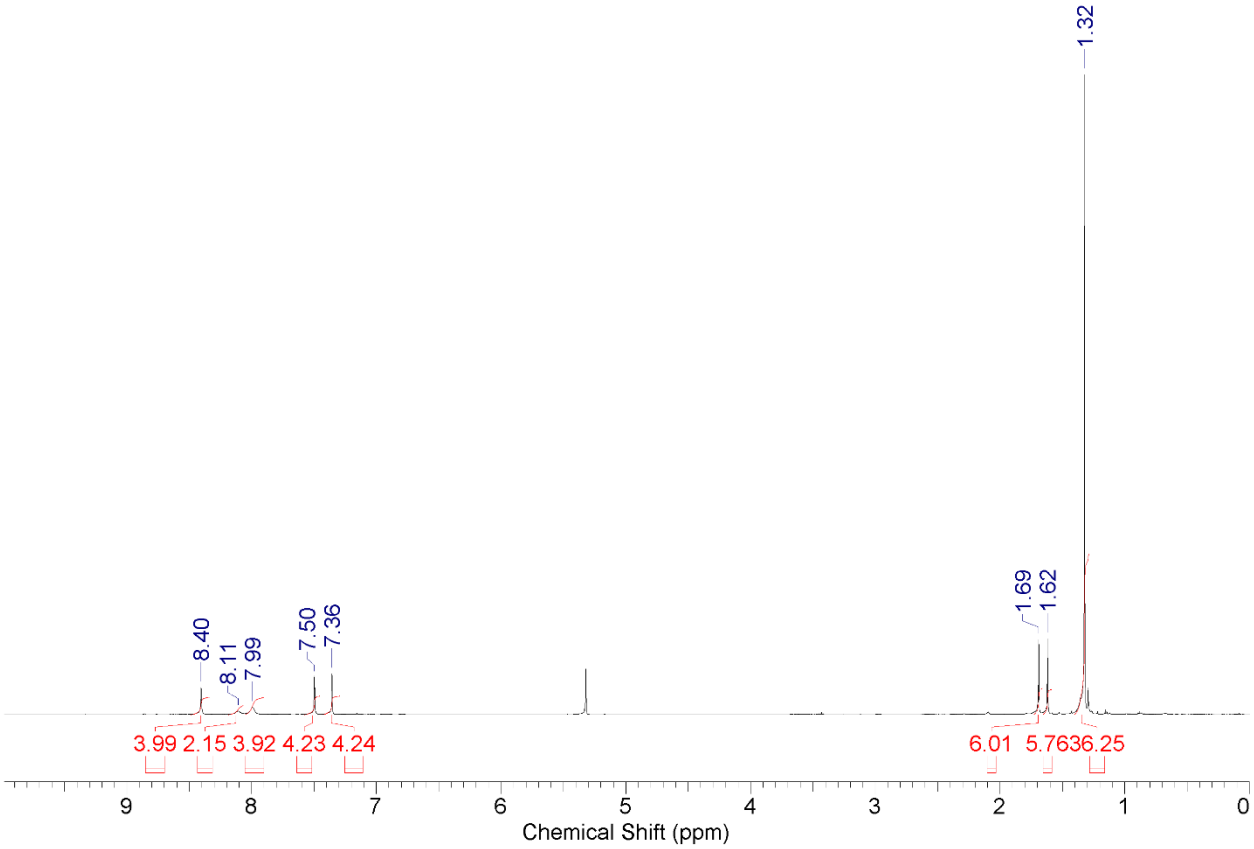

Figure S3: ^{1}H spectrum of **1** (CD_2Cl_2, 600 MHz).

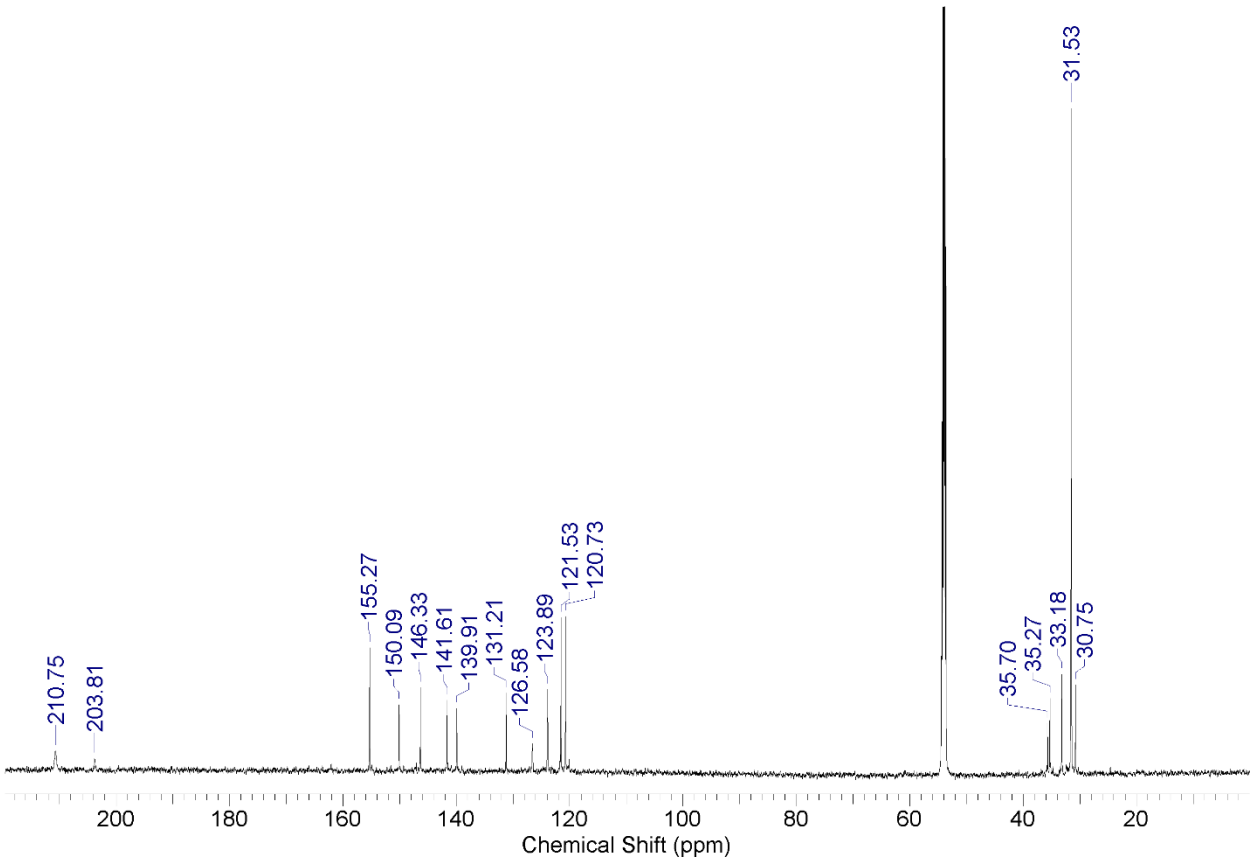

Figure S4: ^{13}C spectrum of **1** (CD_2Cl_2, 150 MHz).

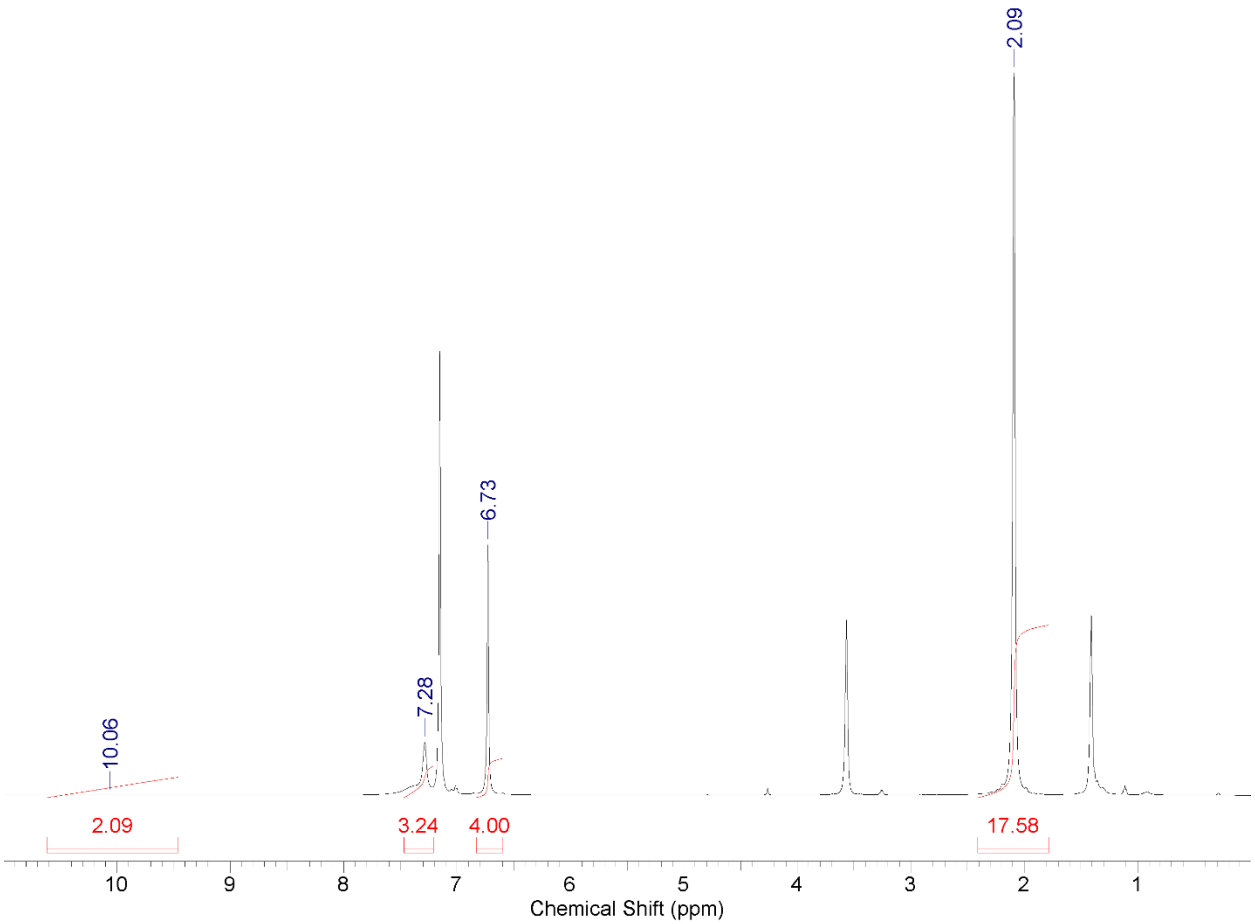

Figure S5: ^{1}H spectrum of **2** (C_6D_6, 600 MHz). The unlabeled peaks correspond to THF.

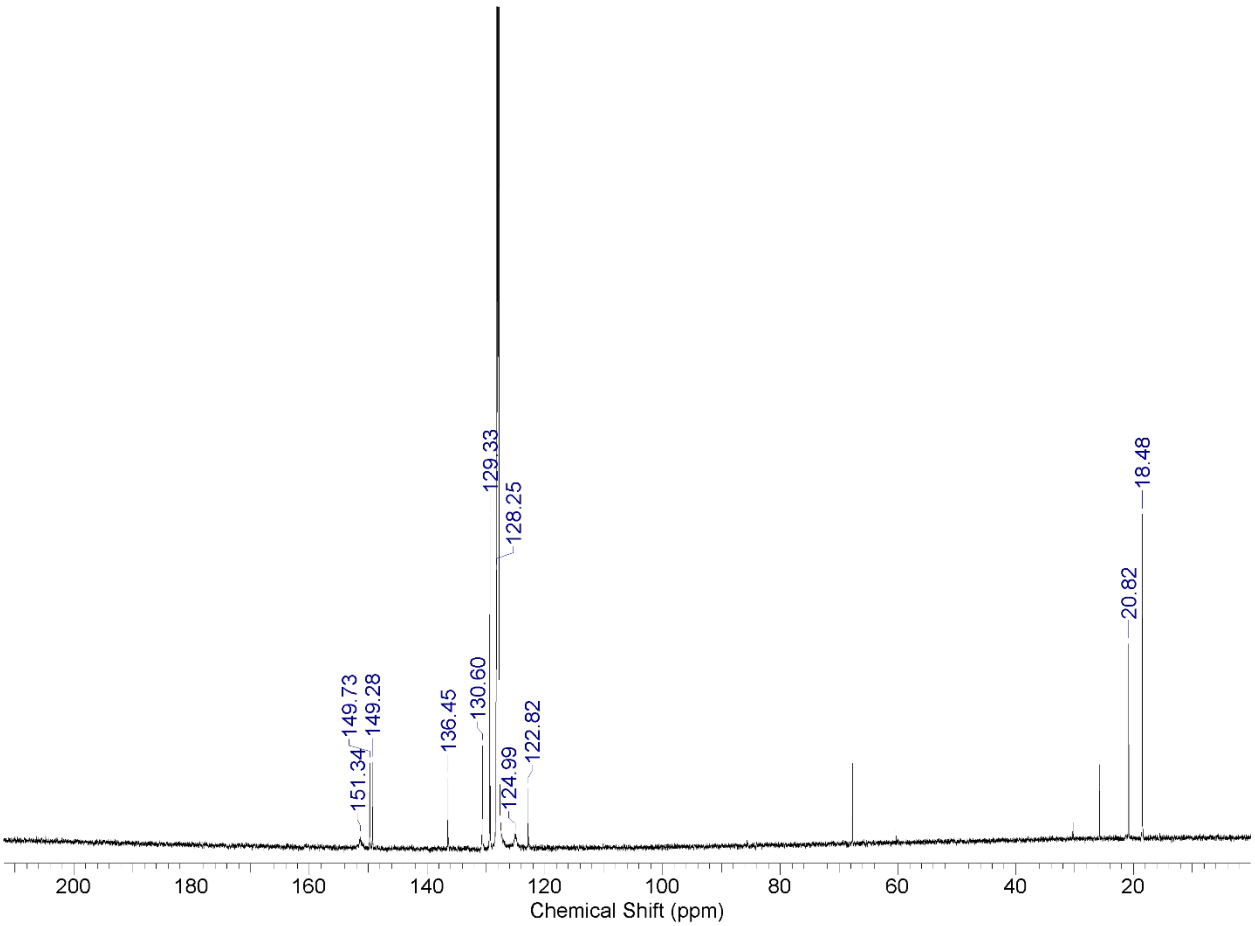

Figure S6: ^{13}C spectrum of **2** (C_6D_6, 150 MHz). The unlabeled peaks correspond to THF.

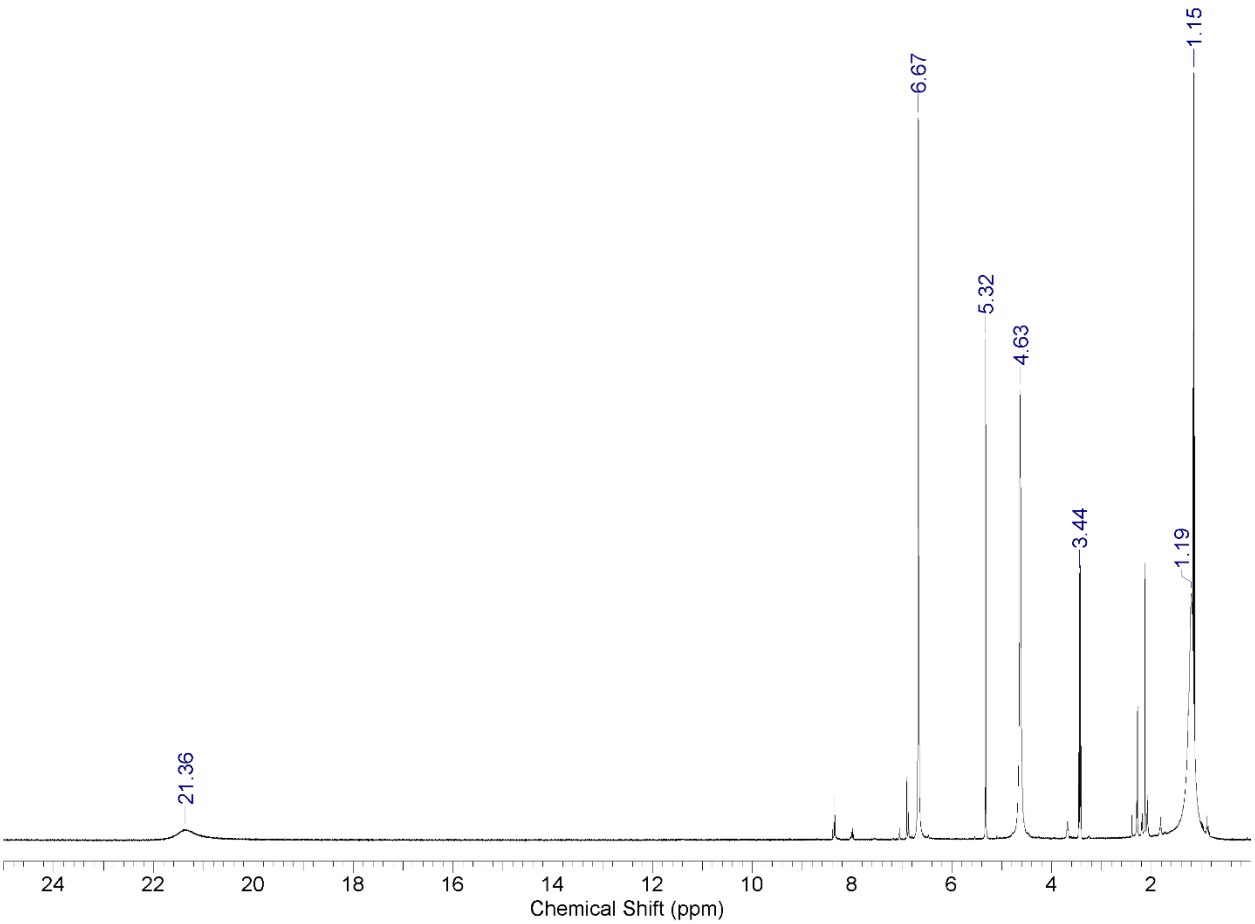

Figure S7: ^{1}H spectrum of **3** (CD_2Cl_2, 400 MHz).

The peaks at 3.44 and 1.15 correspond to ether. The other unlabeled peaks correspond to small quantities of free ligand and **2**.

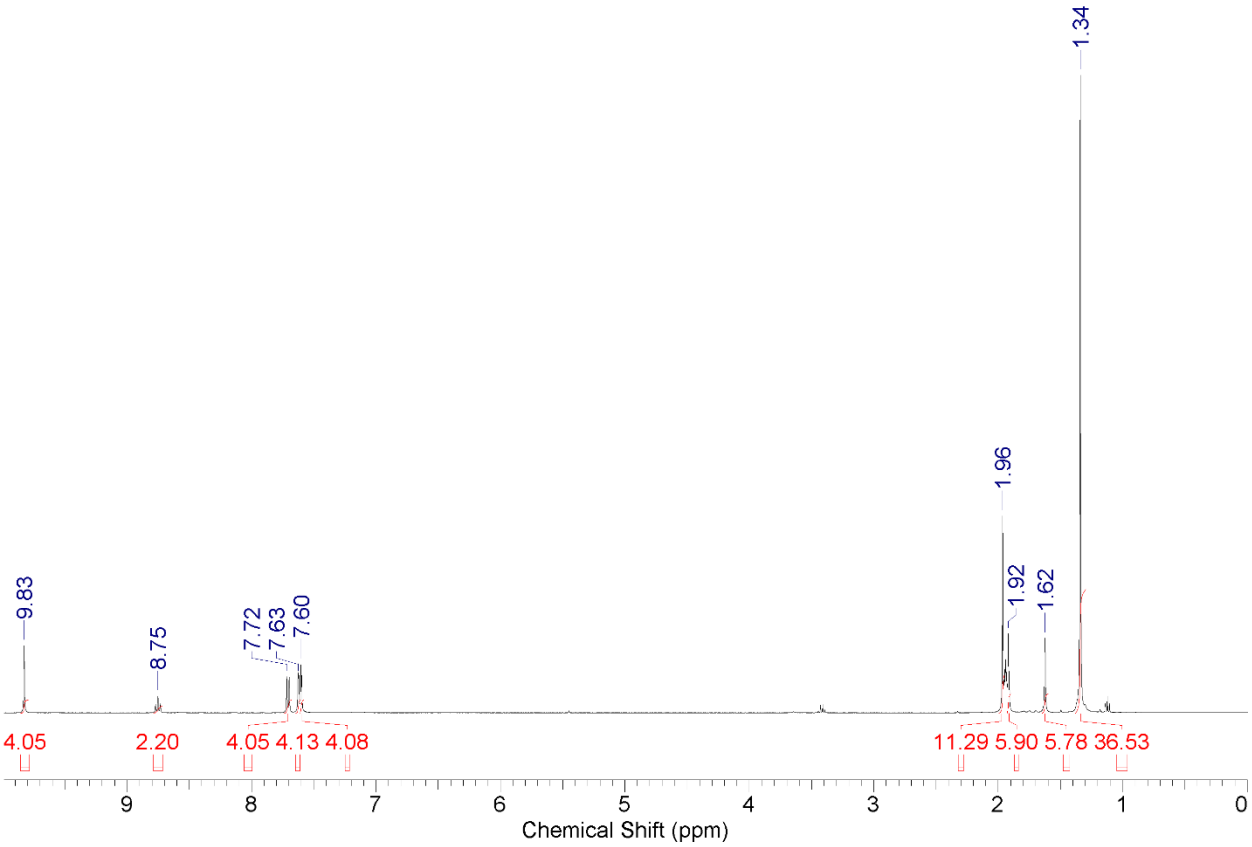

Figure S8: ^{1}H spectrum of **4** (CD_3CN, 600 MHz).

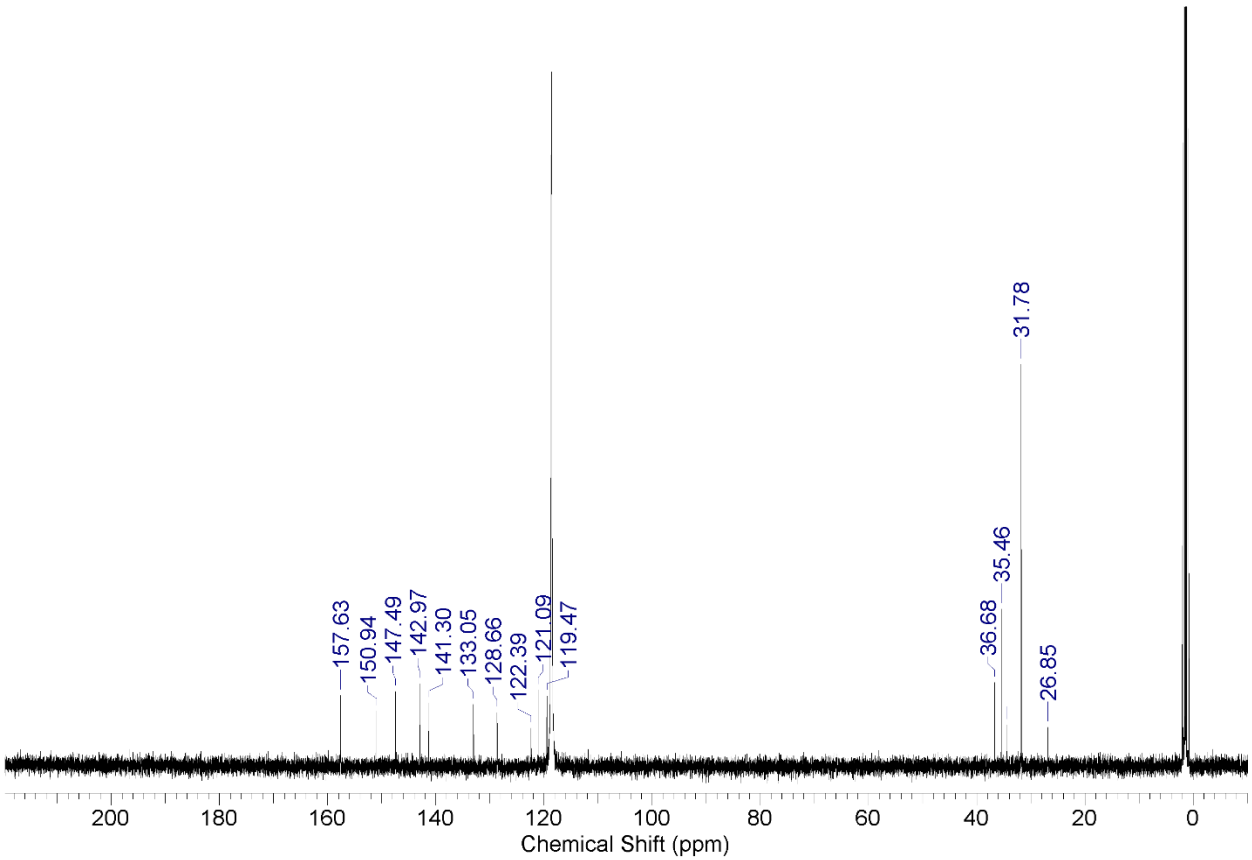

Figure S9: ^{13}C spectrum of **4** (CD_3CN, 150 MHz).

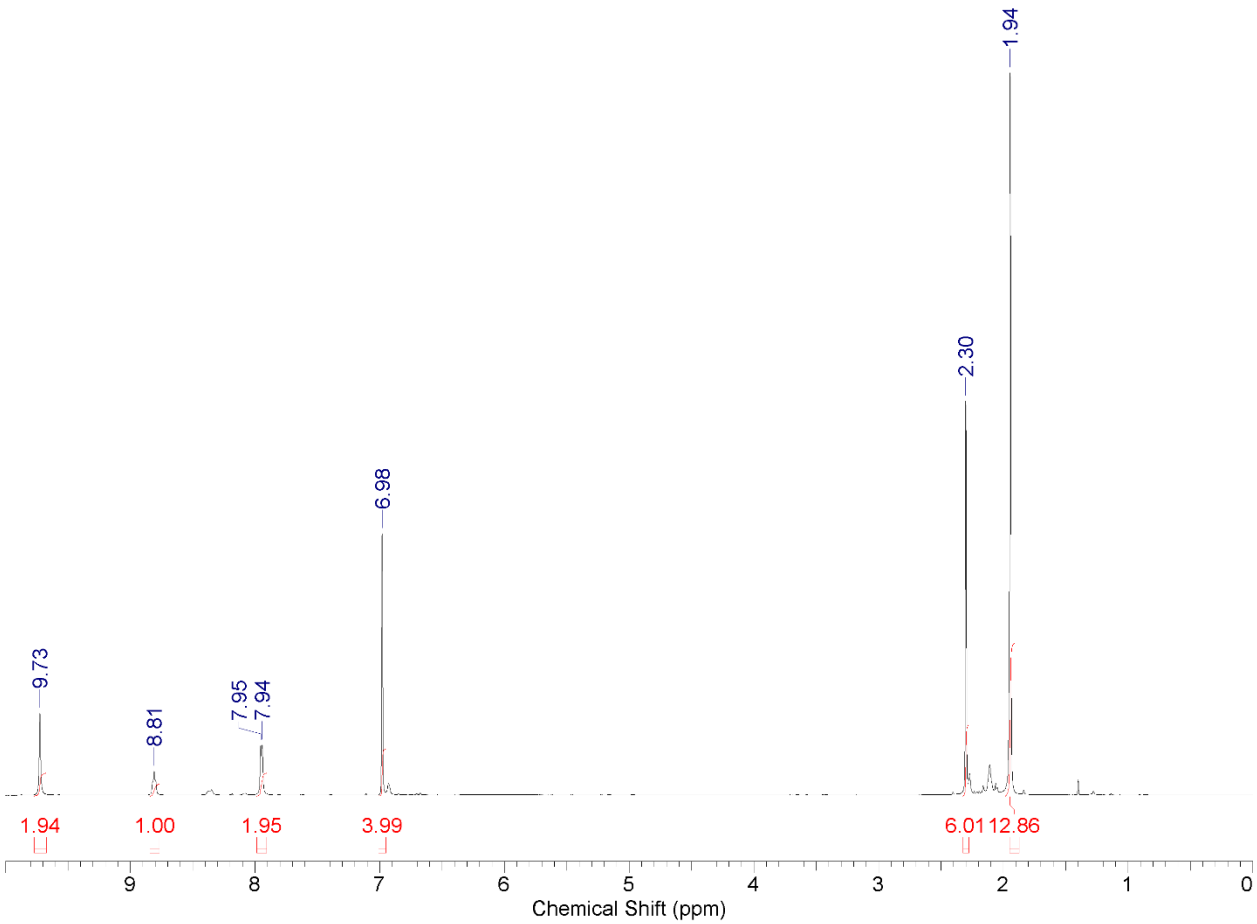

Figure S10: ^{1}H spectrum of **5** (CD_3CN, 600 MHz).

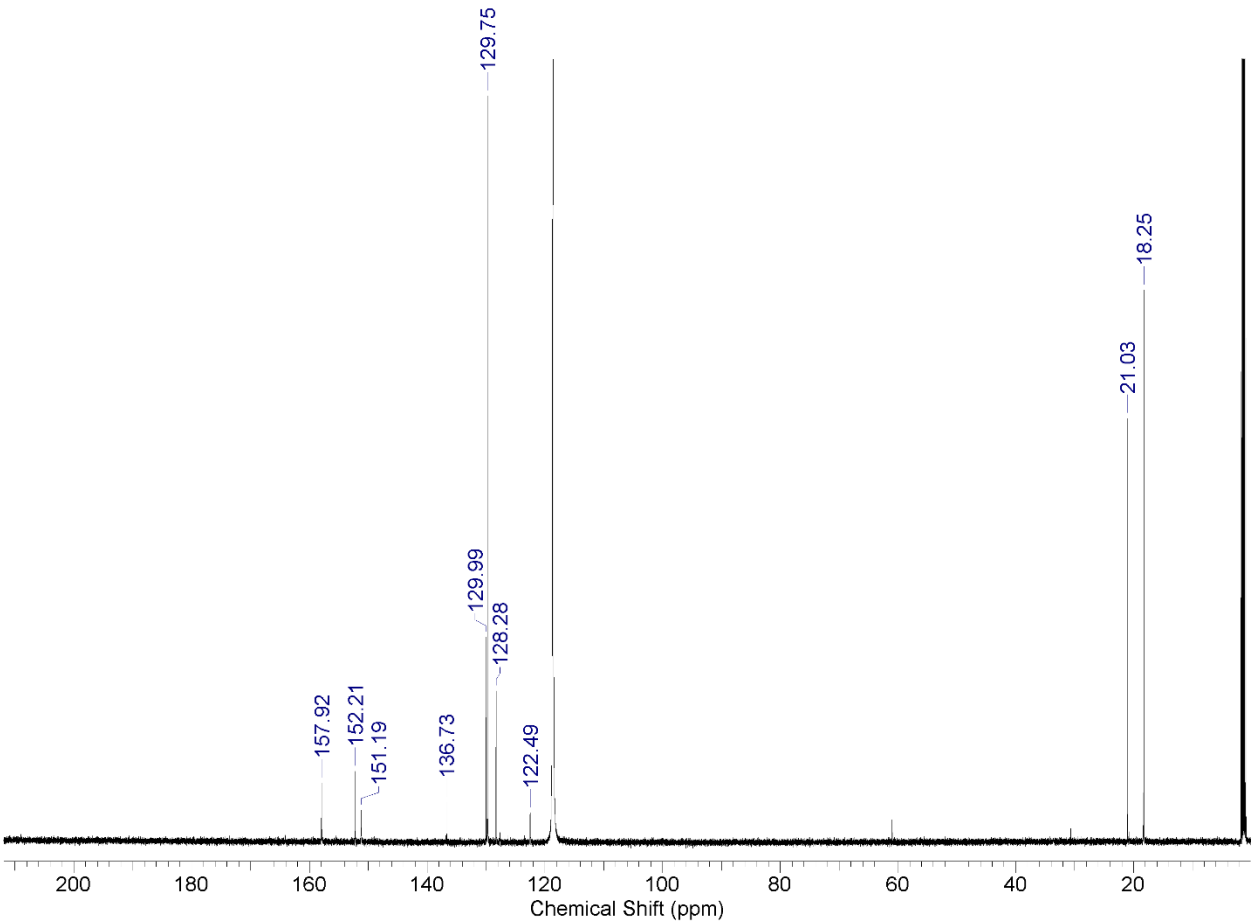

Figure S11: ^{13}C spectrum of **5** (CD_3CN, 150 MHz).

5. UV-Vis Spectra

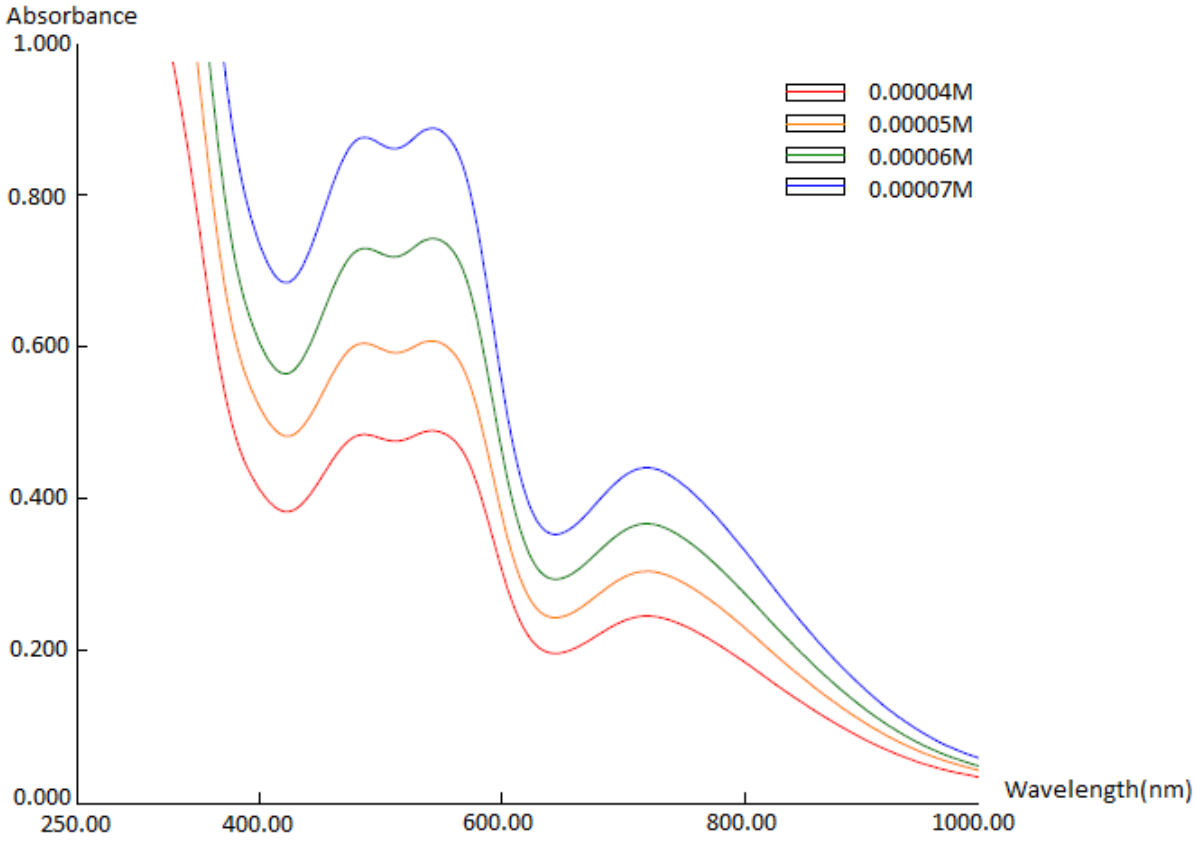

Figure S12: UV-Vis spectrum of **1** at four different concentrations.

$\lambda_{max}(\varepsilon_M)$: 719 (6510), 542 (13350), 487 (13010).

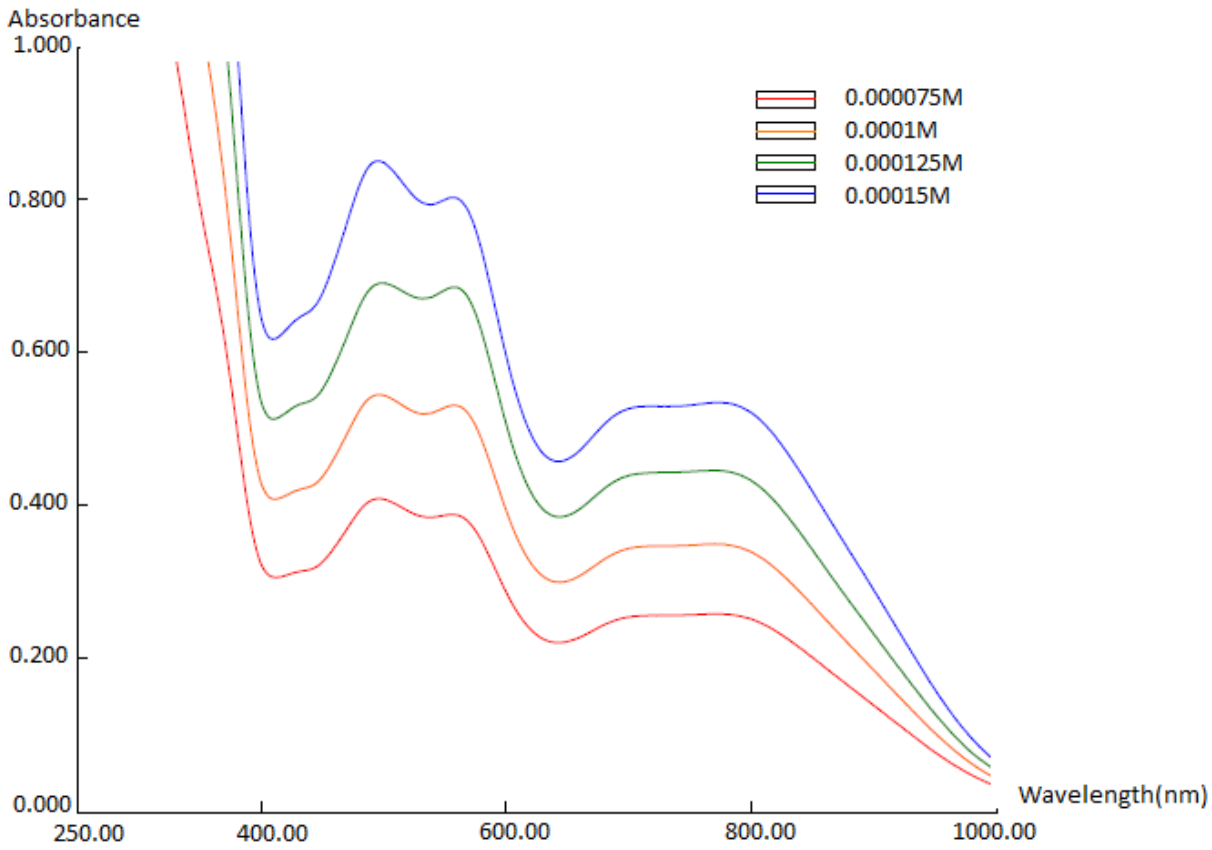

Figure S13: UV-Vis spectrum of **2** at four different concentrations.

$\lambda_{max}(\varepsilon_M)$: 767 (3708), 711 (3672), 556 (5596), 495.5 (5896).

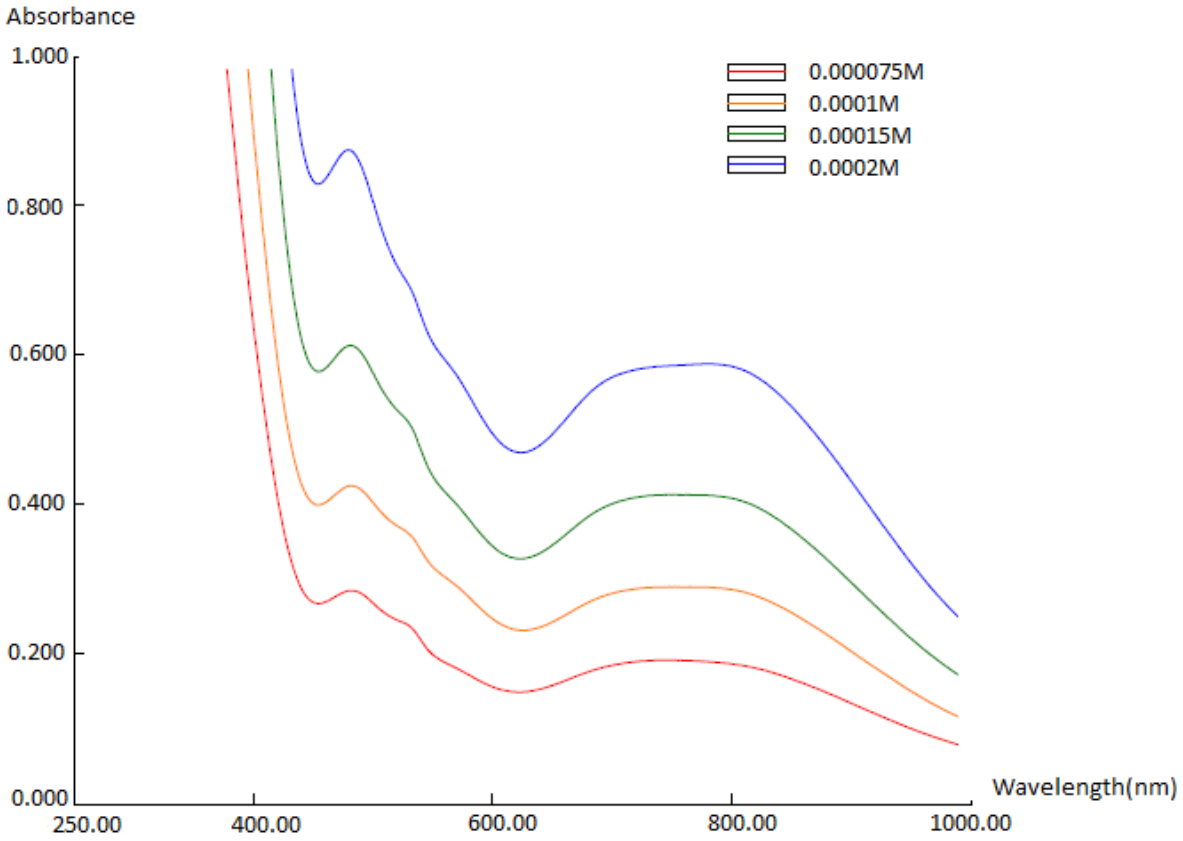

Figure S14: UV-Vis spectrum of **3** at four different concentrations.

$\lambda_{max}(\varepsilon_M)$: 762 (3080), 532.5 (3495), 482(4580).

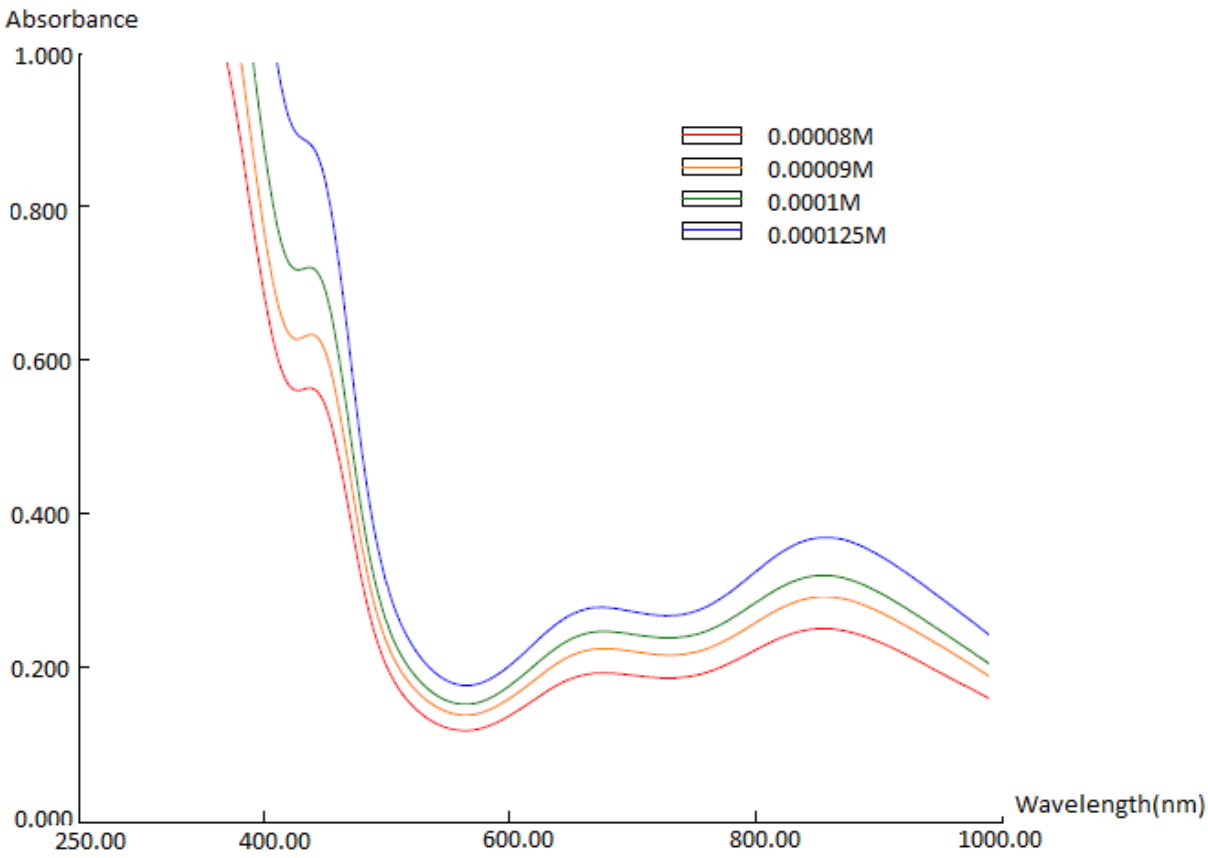

Figure S15: UV-Vis spectrum of **4** at four different concentrations.

$\lambda_{max}(\varepsilon_M)$: 858 (2550), 677 (1830), 439 (7070).

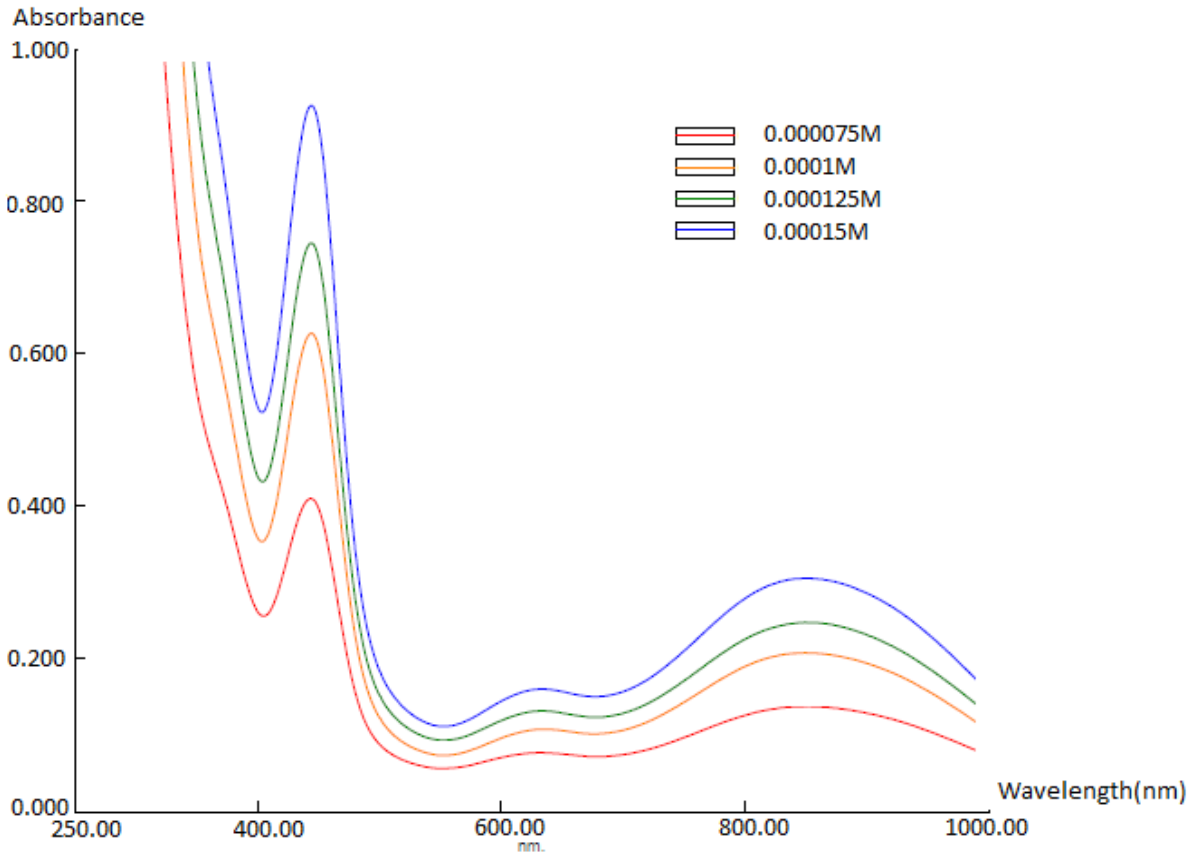

Figure S16: UV-Vis spectrum of **5** at four different concentrations.

$\lambda_{max}(\varepsilon_M)$: 855 (2180), 630.5 (1100), 443.5 (6680).

6. IR Spectra

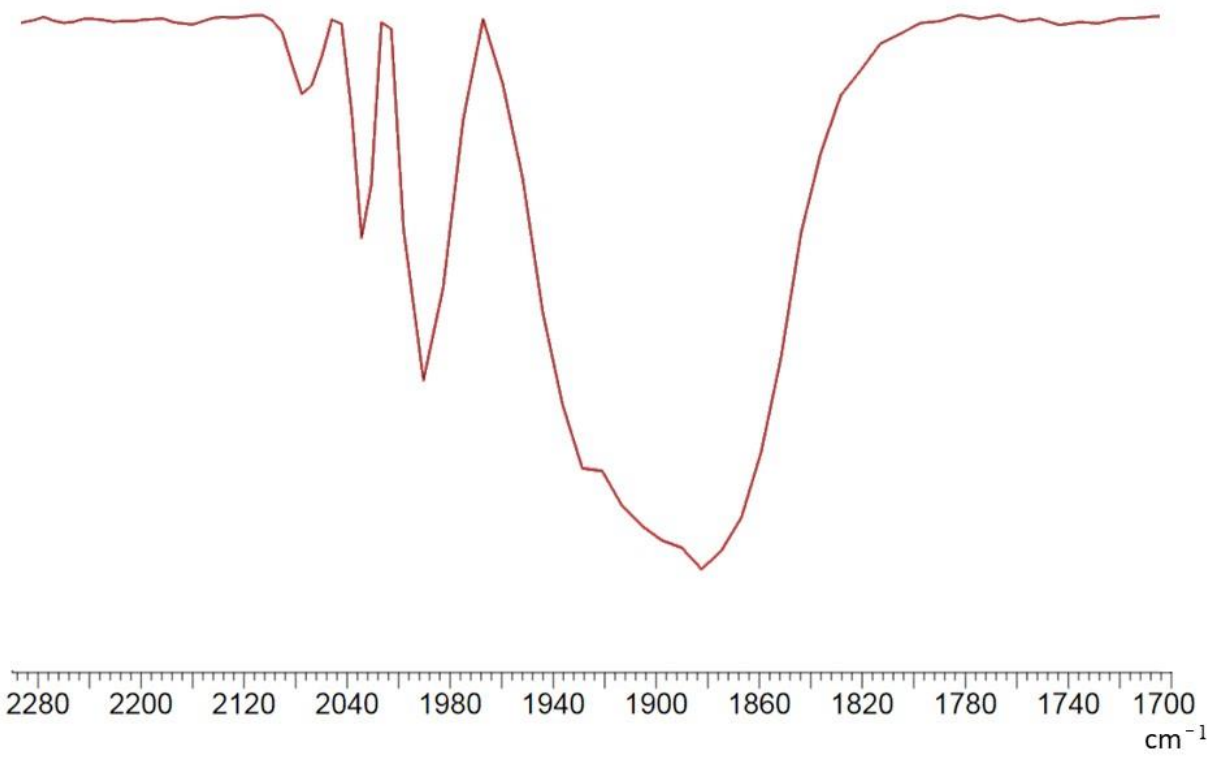

Figure S17: IR spectrum of **1** in the CO region. $\nu_{C\equiv O}$: 2074, 2026, 1990, and 1890 cm^{-1}.

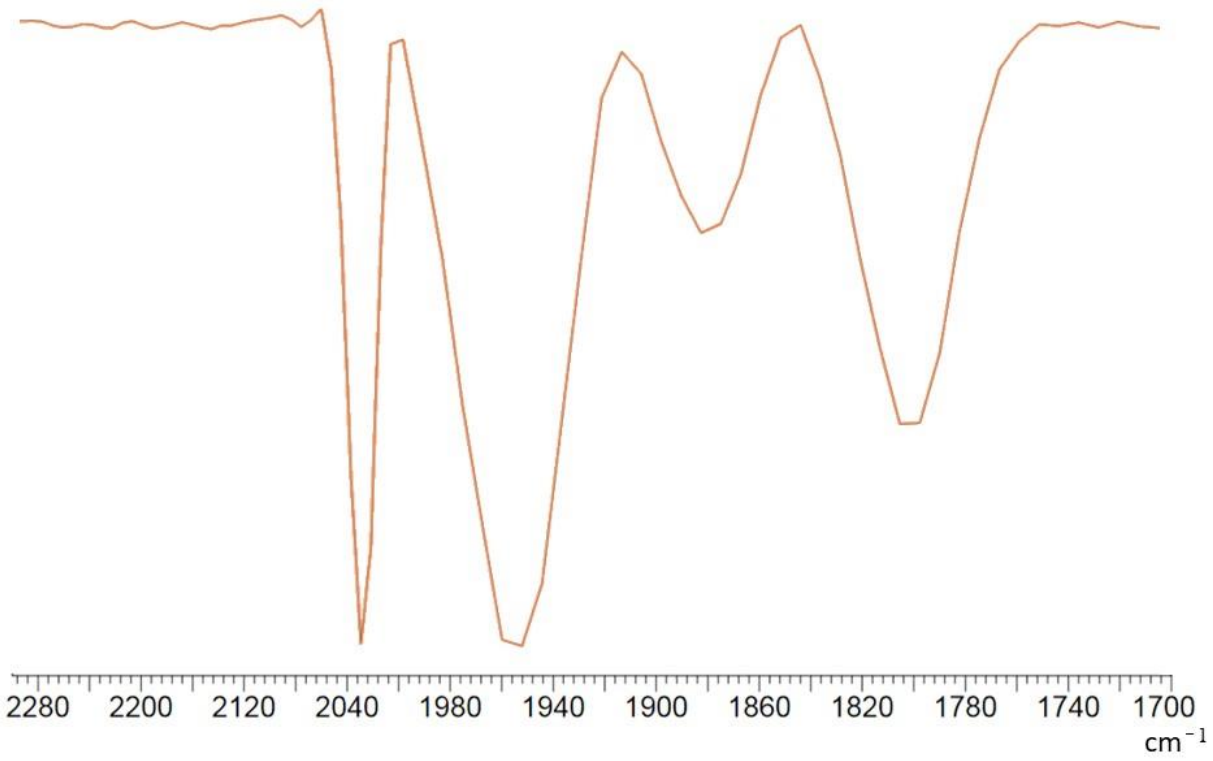

Figure S18: IR spectrum of **2** in the CO region. $\nu_{C\equiv O}$: 2029, 1957, 1880, and 1802 cm^{-1}.

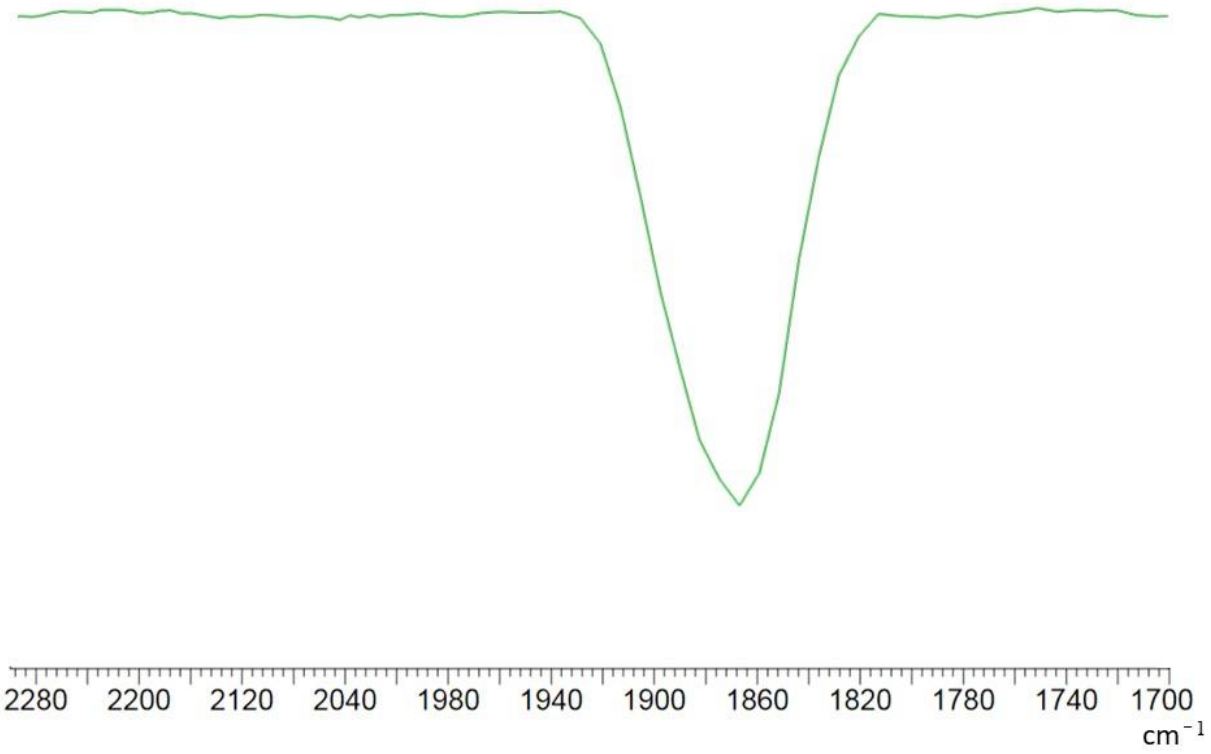

Figure S19: IR spectrum of **3** in the CO region. $\nu_{C\equiv O}$: 1867 cm^{-1}.

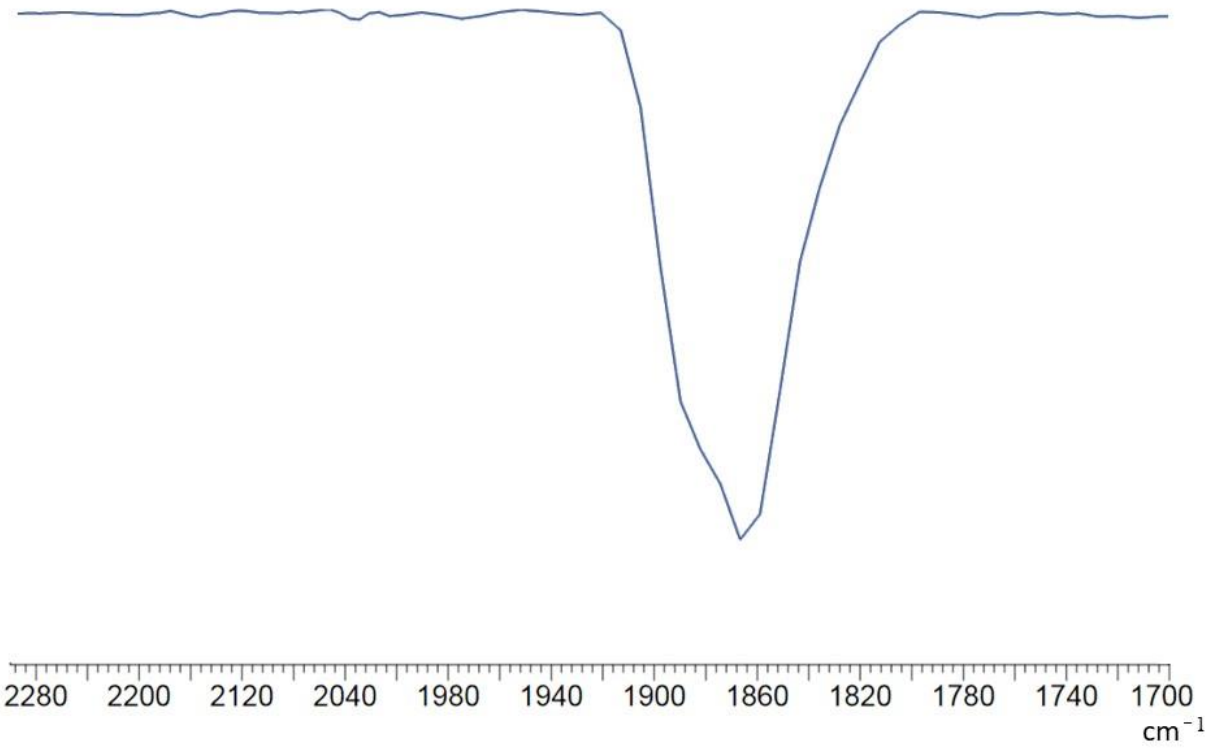

Figure S20: IR spectrum of **4** in the CO region. $\nu_{C\equiv O}$: 1868 cm^{-1}.

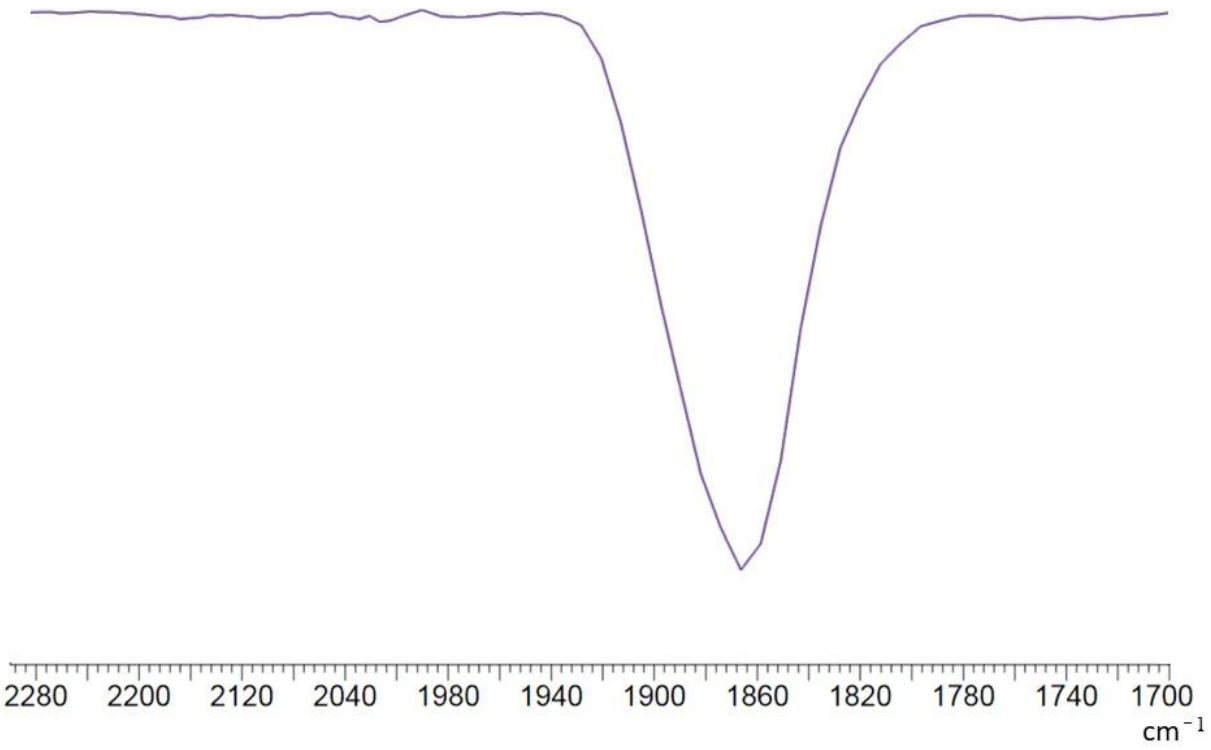

Figure S21: IR spectrum of **5** in the CO region. $\nu_{C\equiv O}$: 1868 cm^{-1}.

7. GC-MS Catalytic Results

General Procedure: 1.00 mmol of ethyl propiolate was added to a 2 mL solution of deuterated solvent, containing 1 or 2 mol% catalyst with 2 mol% internal standard. After completion of the reaction, 0.1 mL of the reaction mixture was diluted 1000-fold in methanol (HPLC) and filtered through a silica plug. GCMS was taken, integrating both arene peaks and the internal standard peak to calculate yield.

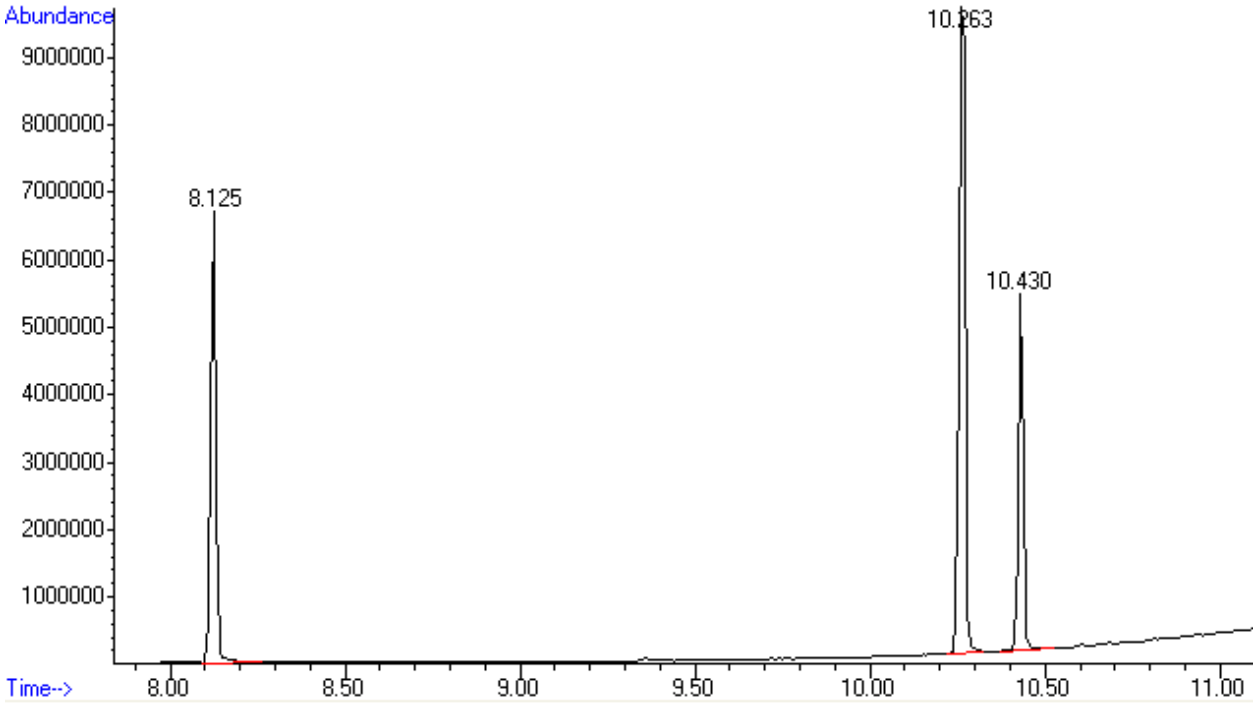

Figure S22: GC-MS spectrum demonstrating arene formation by complex **1** in CD_2Cl_2 at room temperature. The peak at 8.125 corresponds to hexamethylbenzene, the peak at 10.263 corresponds to the 1,2,4-isomer, and the peak at 10.430 corresponds to the 1,3,5-isomer.

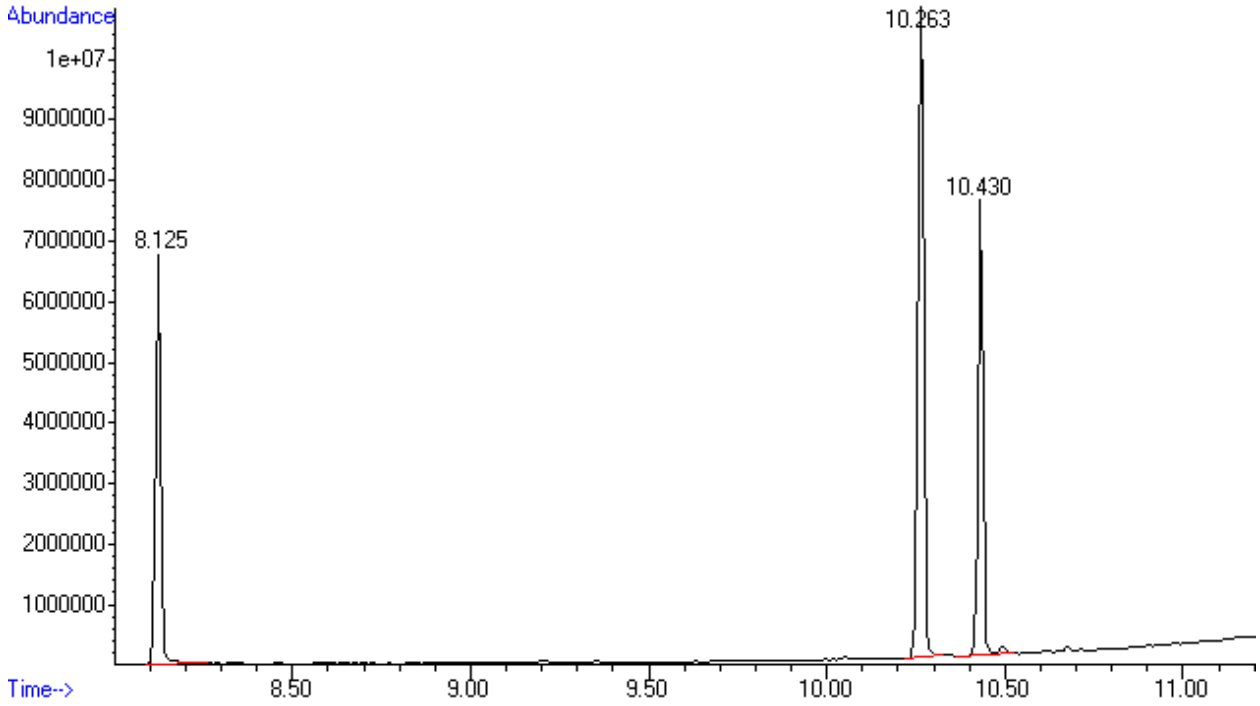

Figure S23: GC-MS spectrum demonstrating arene formation by complex **2** in CD_2Cl_2 at room temperature. The peak at 8.125 corresponds to hexamethylbenzene, the peak at 10.263 corresponds to the 1,2,4-isomer, and the peak at 10.430 corresponds to the 1,3,5-isomer.

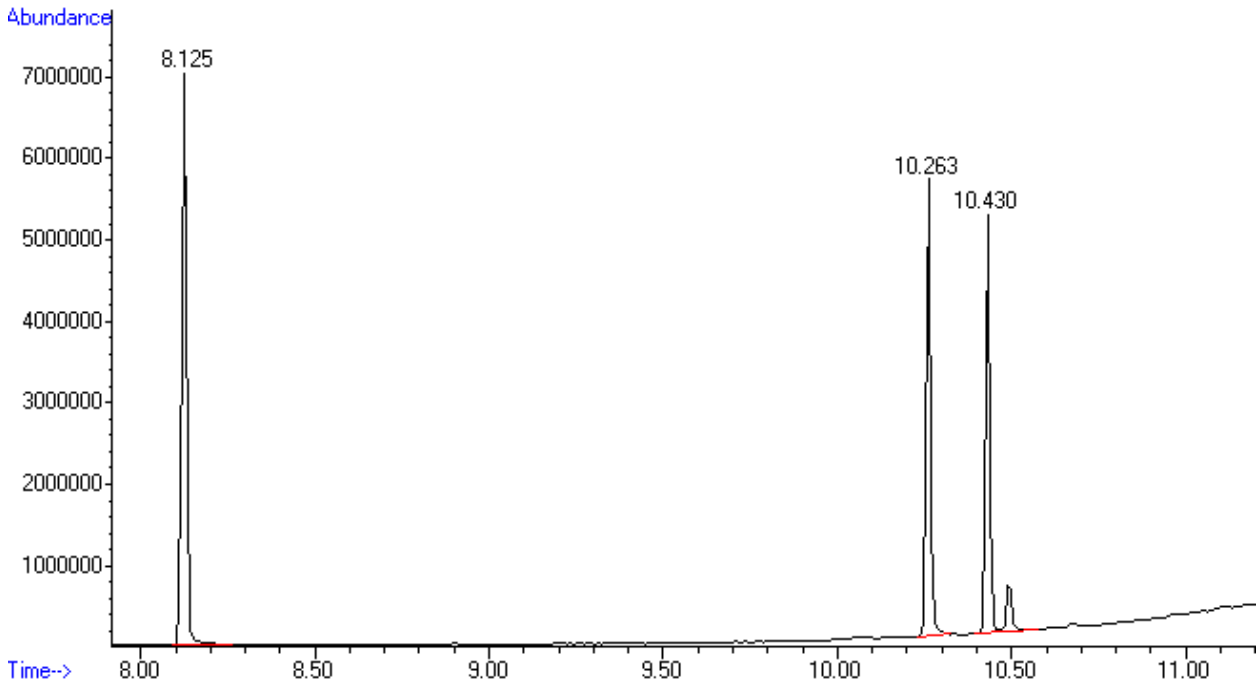

Figure S24: GC-MS spectrum demonstrating arene formation by complex **3** in CD_2Cl_2 at room temperature. The peak at 8.125 corresponds to hexamethylbenzene, the peak at 10.263 corresponds to the 1,2,4-isomer, and the peak at 10.430 corresponds to the 1,3,5-isomer.

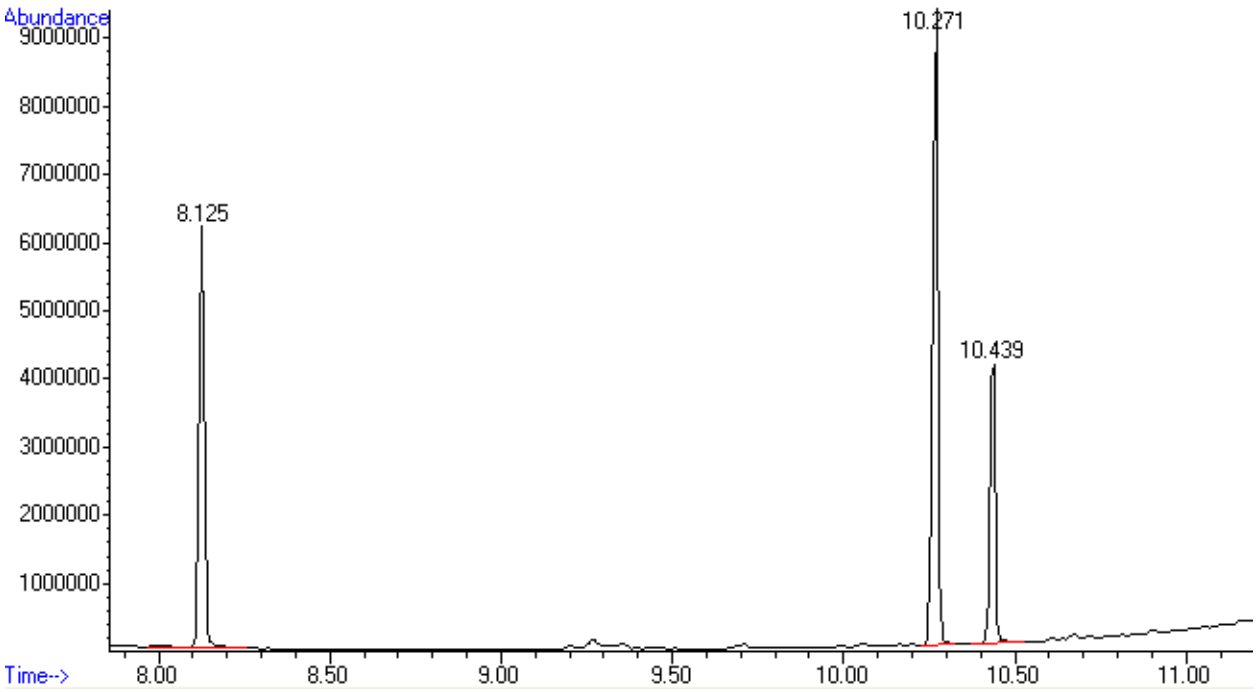

Figure S25: GC-MS spectrum demonstrating arene formation by complex **4** in CD_2Cl_2 at room temperature. The peak at 8.125 corresponds to hexamethylbenzene, the peak at 10.271 corresponds to the 1,2,4-isomer, and the peak at 10.439 corresponds to the 1,3,5-isomer.

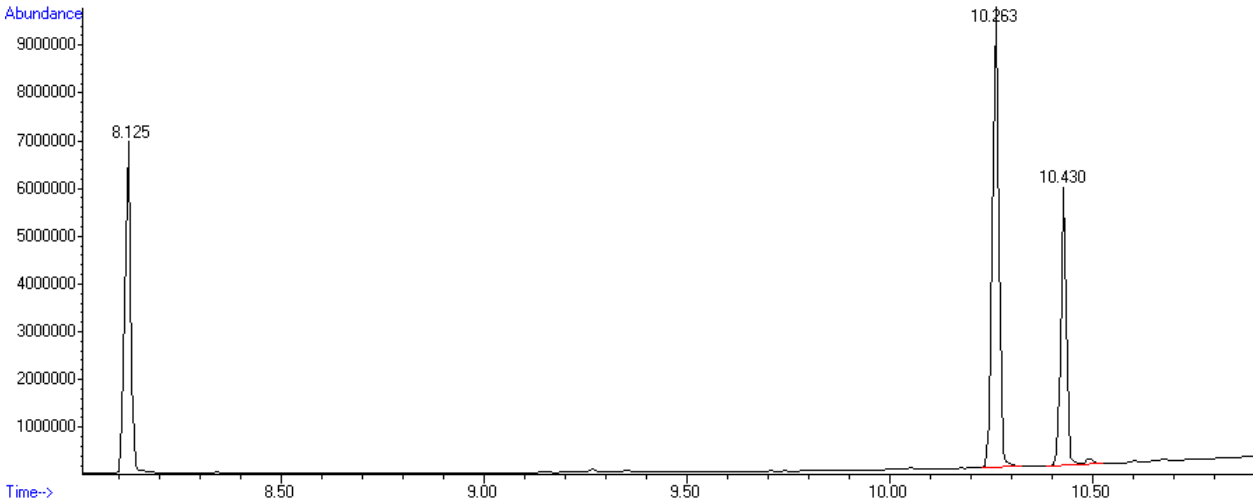

Figure S26: GC-MS spectrum demonstrating arene formation by complex **5** in CD_2Cl_2 at room temperature. The peak at 8.125 corresponds to hexamethylbenzene, the peak at 10.263 corresponds to the 1,2,4-isomer, and the peak at 10.430 corresponds to the 1,3,5-isomer.

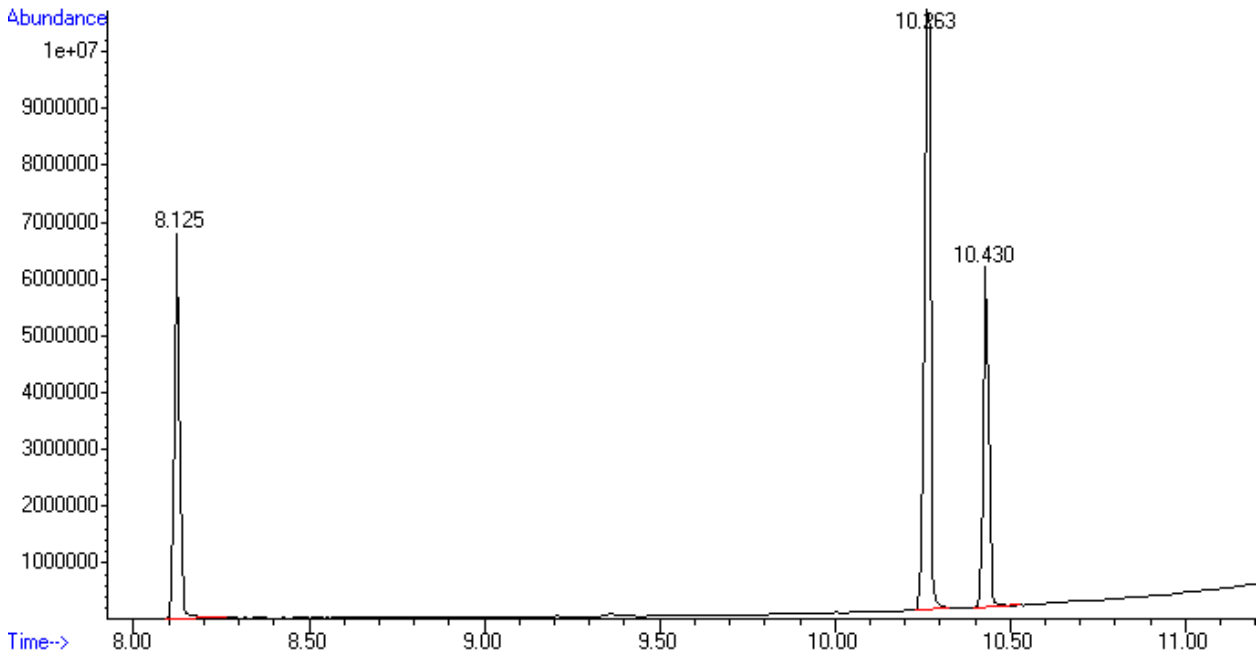

Figure S27: GC-MS spectrum demonstrating arene formation by $Co_2(CO)_8$ in CD_2Cl_2 at room temperature. The peak at 8.125 corresponds to hexamethylbenzene, the peak at 10.263 corresponds to the 1,2,4-isomer, and the peak at 10.430 corresponds to the 1,3,5-isomer.

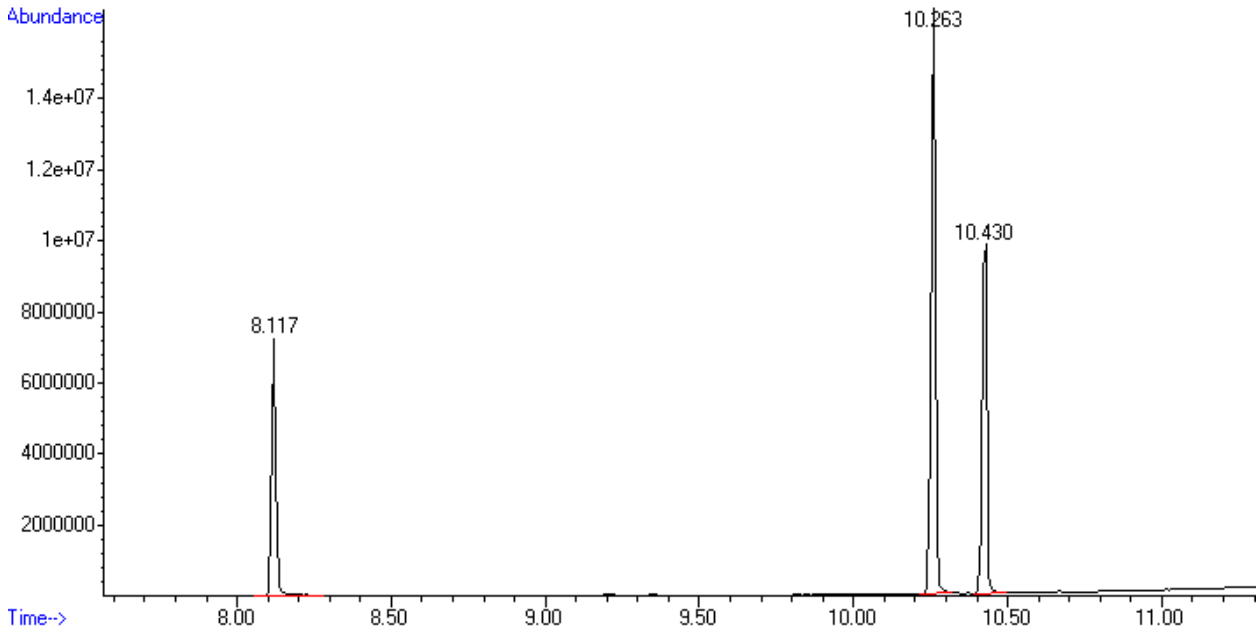

Figure S28: GC-MS spectrum demonstrating arene formation by complex **1** in CD_2Cl_2 at 40 °C. The peak at 8.117 corresponds to hexamethylbenzene, the peak at 10.263 corresponds to the 1,2,4-isomer, and the peak at 10.430 corresponds to the 1,3,5-isomer.

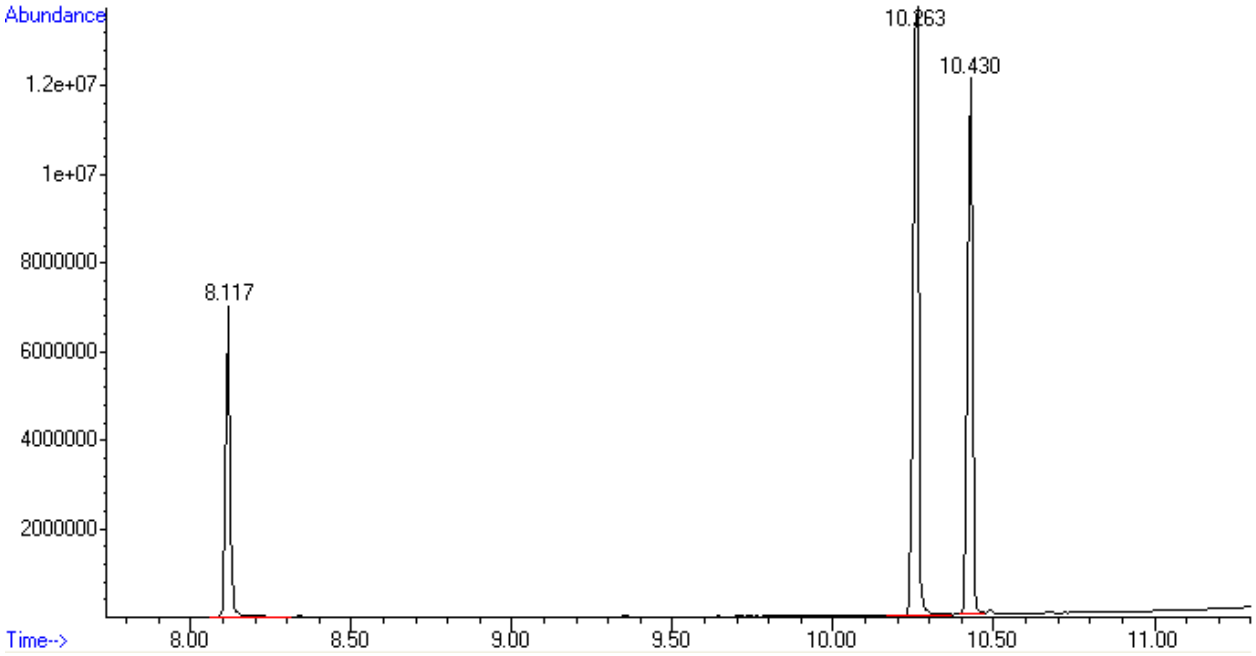

Figure S29: GC-MS spectrum demonstrating arene formation by complex **2** in CD_2Cl_2 at 40 °C. The peak at 8.117 corresponds to hexamethylbenzene, the peak at 10.263 corresponds to the 1,2,4-isomer, and the peak at 10.430 corresponds to the 1,3,5-isomer.

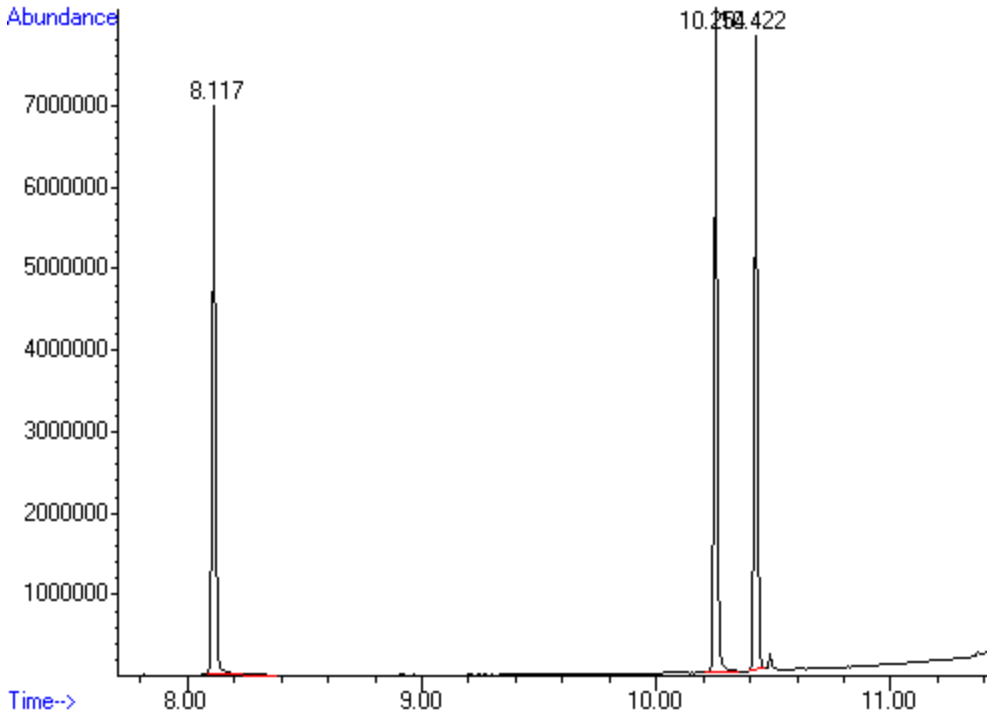

Figure S30: GC-MS spectrum demonstrating arene formation by complex **3** in CD_2Cl_2 at 40 °C. The peak at 8.117 corresponds to hexamethylbenzene, the peak at 10.254 corresponds to the 1,2,4-isomer, and the peak at 10.422 corresponds to the 1,3,5-isomer.

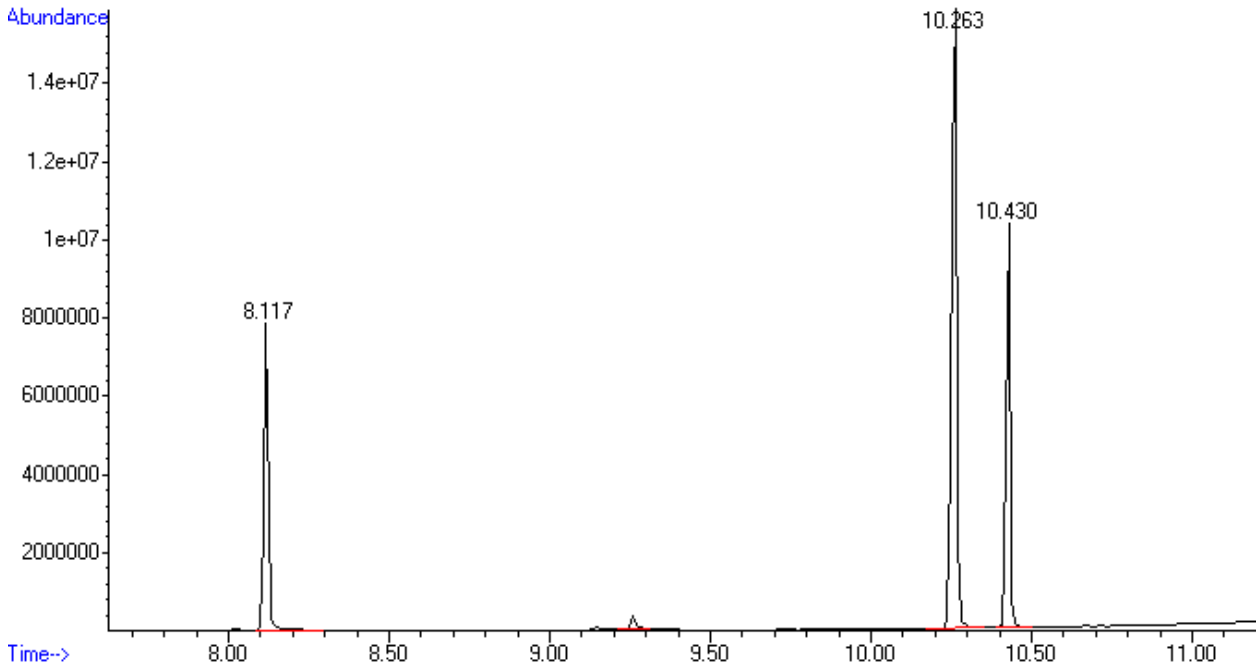

Figure S31: GC-MS spectrum demonstrating arene formation by complex **4** in CD_2Cl_2 at 40 °C. The peak at 8.117 corresponds to hexamethylbenzene, the peak at 10.263 corresponds to the 1,2,4-isomer, and the peak at 10.430 corresponds to the 1,3,5-isomer.

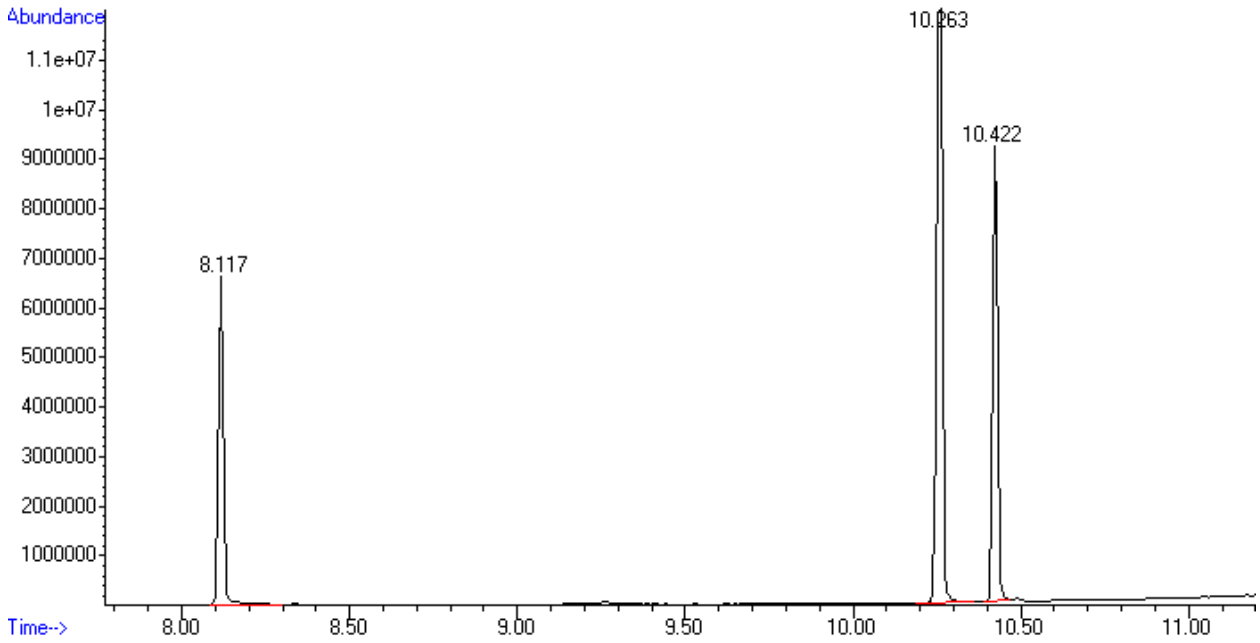

Figure S32: GC-MS spectrum demonstrating arene formation by complex **5** in CD_2Cl_2 at 40 °C. The peak at 8.117 corresponds to hexamethylbenzene, the peak at 10.263 corresponds to the 1,2,4-isomer, and the peak at 10.422 corresponds to the 1,3,5-isomer.

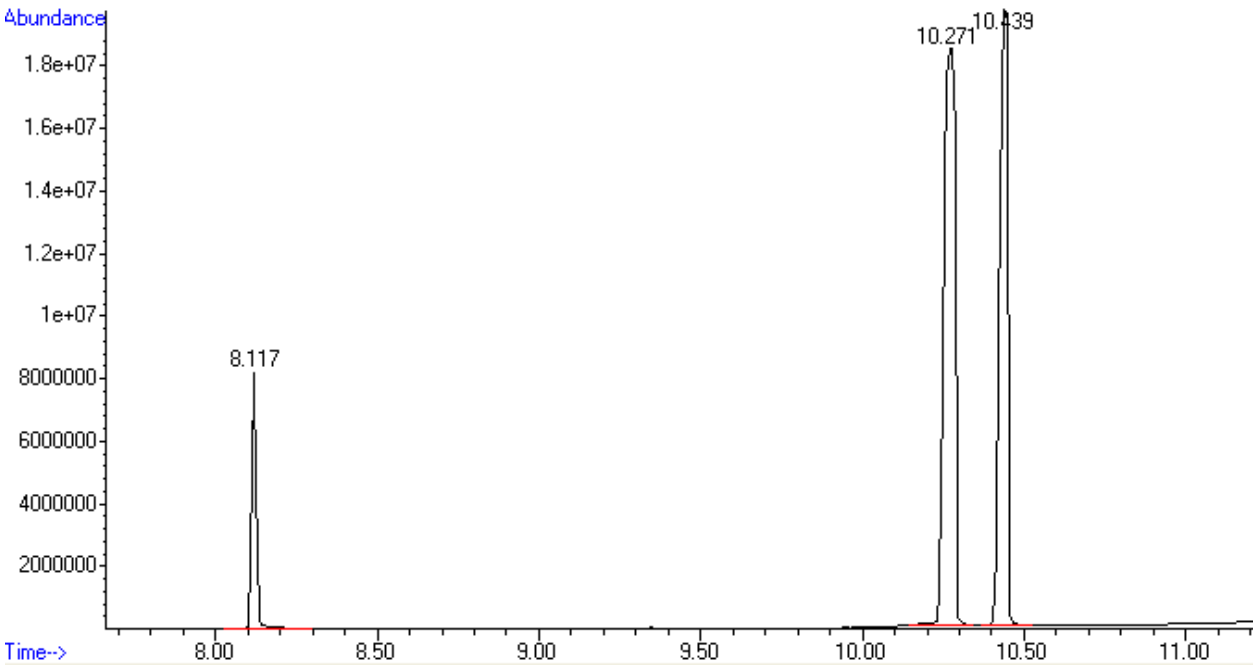

Figure S33: GC-MS spectrum demonstrating arene formation by $Co_2(CO)_8$ at 40 °C. The peak at 8.117 corresponds to hexamethylbenzene, the peak at 10.271 corresponds to the 1,2,4-isomer, and the peak at 10.439 corresponds to the 1,3,5-isomer.

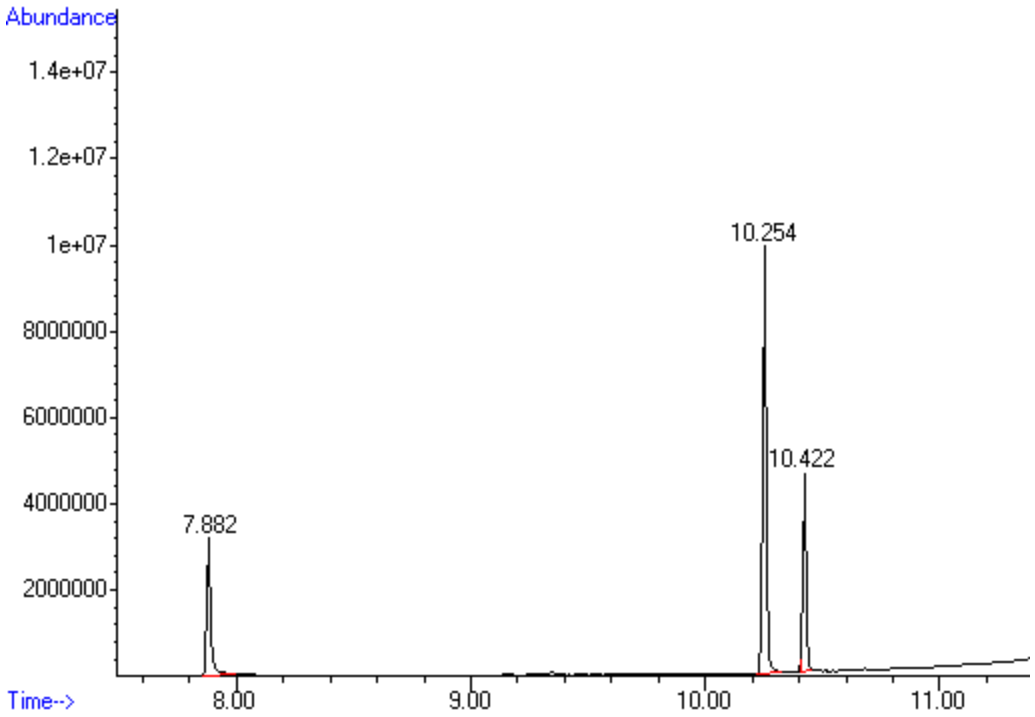

Figure S34: GC-MS spectrum demonstrating arene formation by complex **1** in C_7D_8 at room temperature. The peak at 7.882 corresponds to 1,3,5-trimethoxybenzene, the peak at 10.254 corresponds to the 1,2,4-isomer, and the peak at 10.422 corresponds to the 1,3,5-isomer.

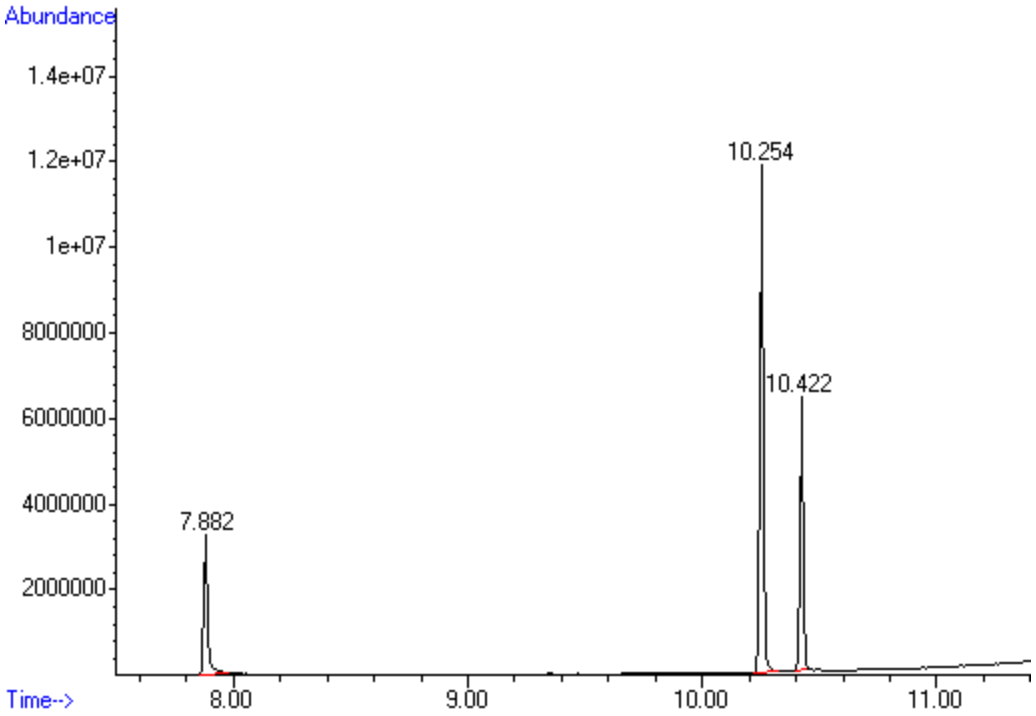

Figure S35: GC-MS spectrum demonstrating arene formation by complex **2** in C_7D_8 at room temperature. The peak at 7.882 corresponds to 1,3,5-trimethoxybenzene, the peak at 10.254 corresponds to the 1,2,4-isomer, and the peak at 10.422 corresponds to the 1,3,5-isomer.

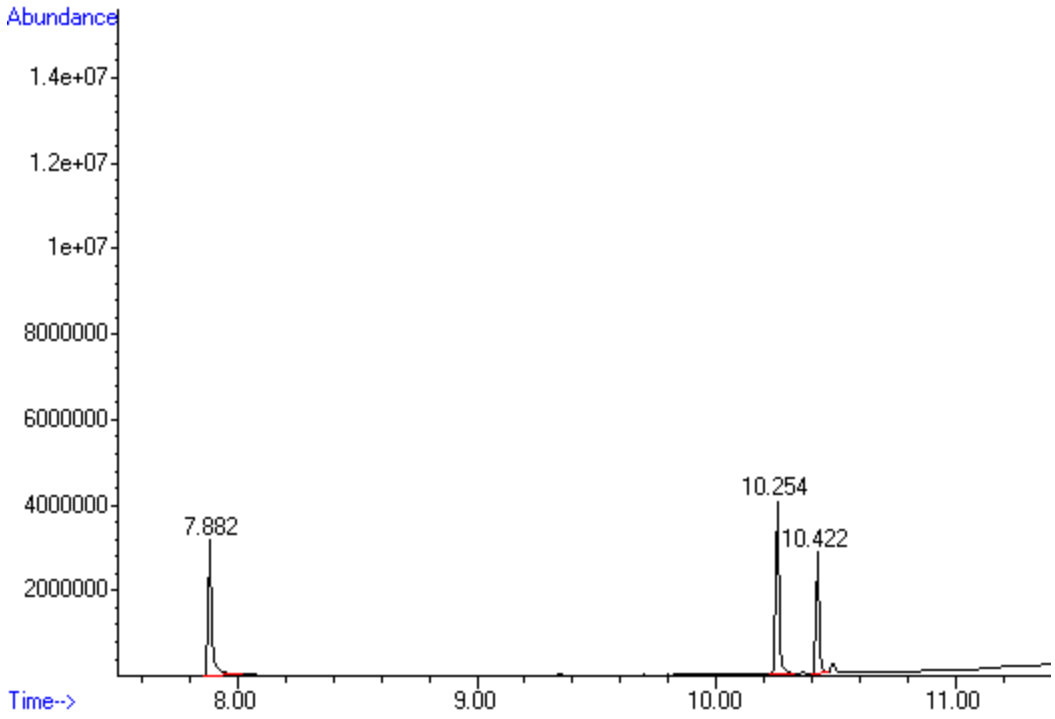

Figure S36: GC-MS spectrum demonstrating arene formation by complex **3** in C_7D_8 at room temperature. The peak at 7.882 corresponds to 1,3,5-trimethoxybenzene, the peak at 10.254 corresponds to the 1,2,4-isomer, and the peak at 10.422 corresponds to the 1,3,5-isomer.

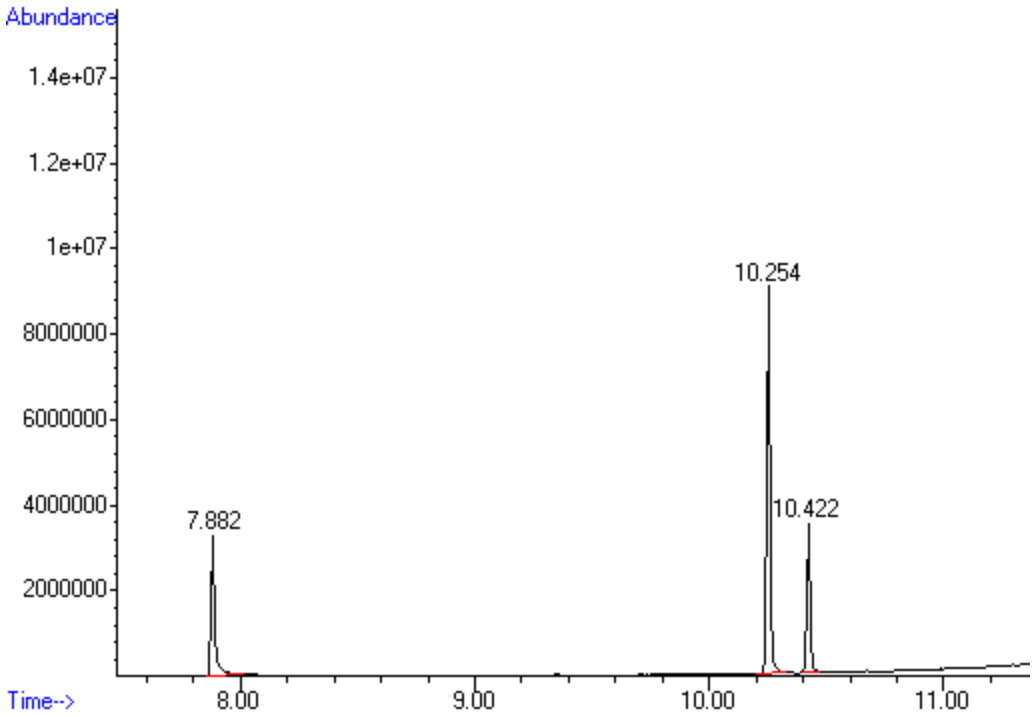

Figure S37: GC-MS spectrum demonstrating arene formation by complex **4** in C_7D_8 at room temperature. The peak at 7.882 corresponds to 1,3,5-trimethoxybenzene, the peak at 10.254 corresponds to the 1,2,4-isomer, and the peak at 10.422 corresponds to the 1,3,5-isomer.

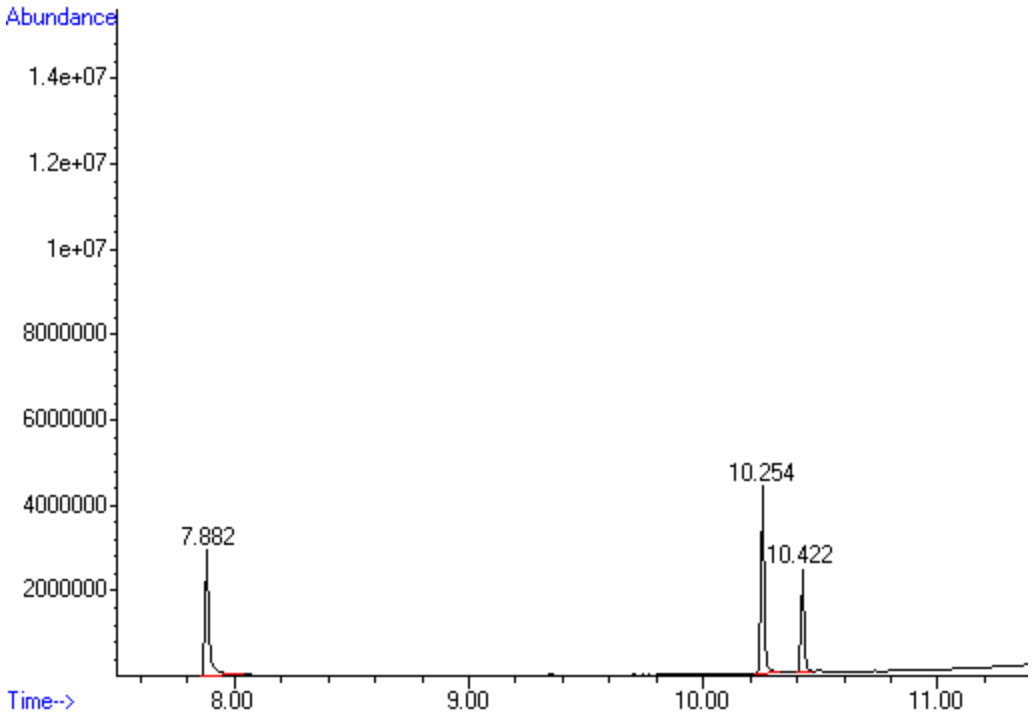

Figure S38: GC-MS spectrum demonstrating arene formation by complex **5** in C_7D_8 at room temperature. The peak at 7.882 corresponds to 1,3,5-trimethoxybenzene, the peak at 10.254 corresponds to the 1,2,4-isomer, and the peak at 10.422 corresponds to the 1,3,5-isomer.

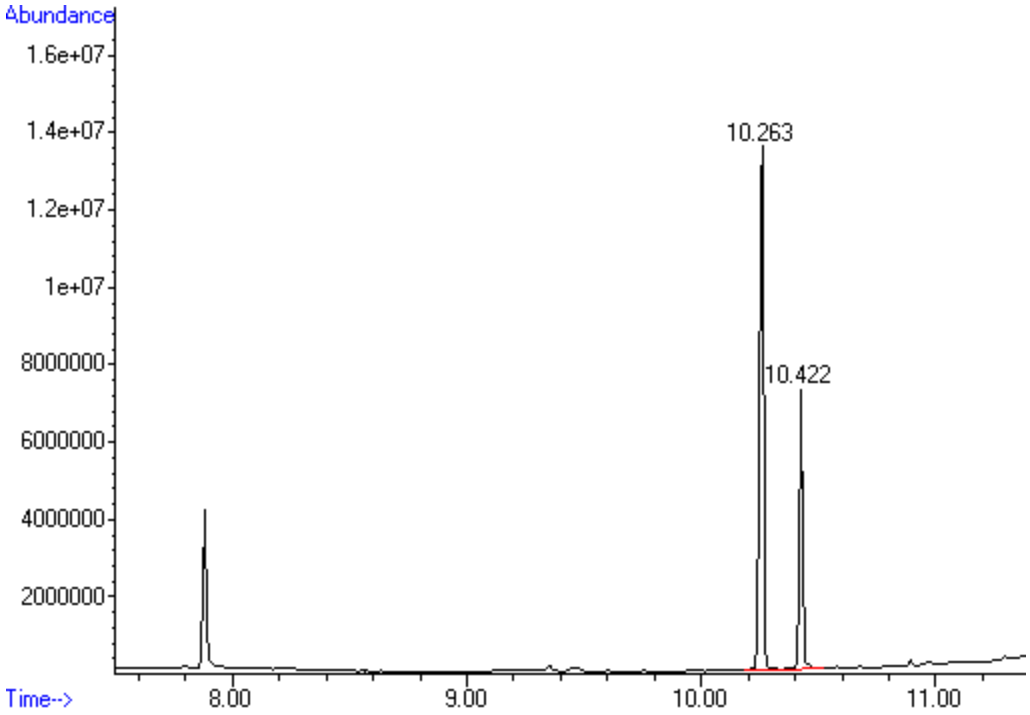

Figure S39: GC-MS spectrum demonstrating arene formation by $Co_2(CO)_8$ in C_7D_8 at room temperature. The peak at 7.882 corresponds to 1,3,5-trimethoxybenzene, the peak at 10.263 corresponds to the 1,2,4-isomer, and the peak at 10.422 corresponds to the 1,3,5-isomer.

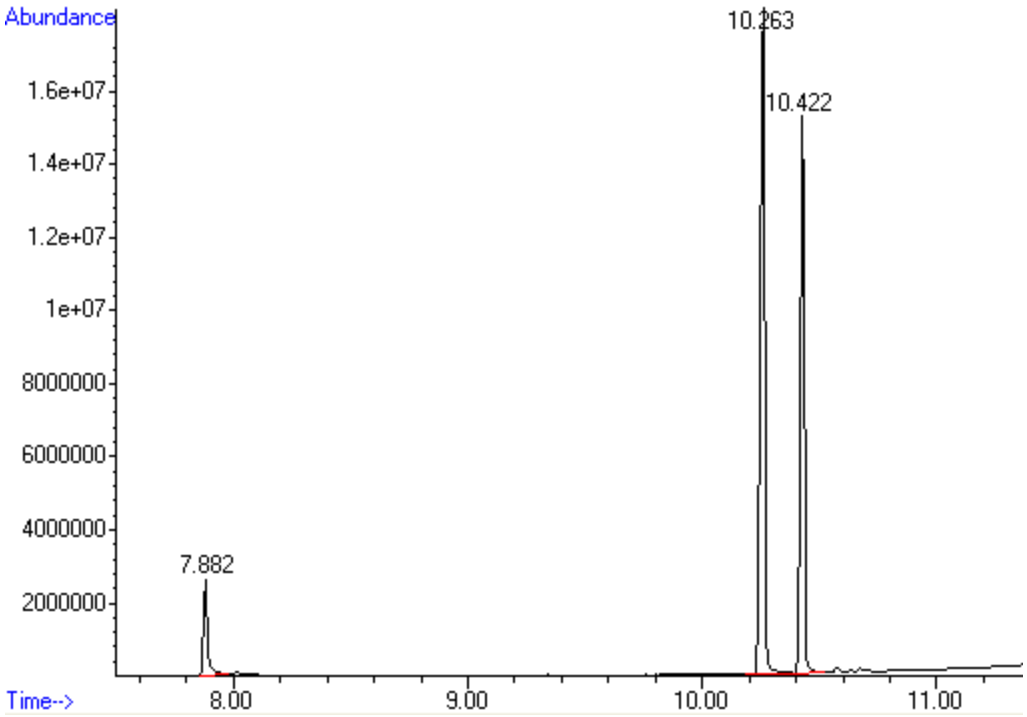

Figure S40: GC-MS spectrum demonstrating arene formation by complex **1** in C_7D_8 at 80 °C. The peak at 7.882 corresponds to 1,3,5-trimethoxybenzene, the peak at 10.263 corresponds to the 1,2,4-isomer, and the peak at 10.422 corresponds to the 1,3,5-isomer.

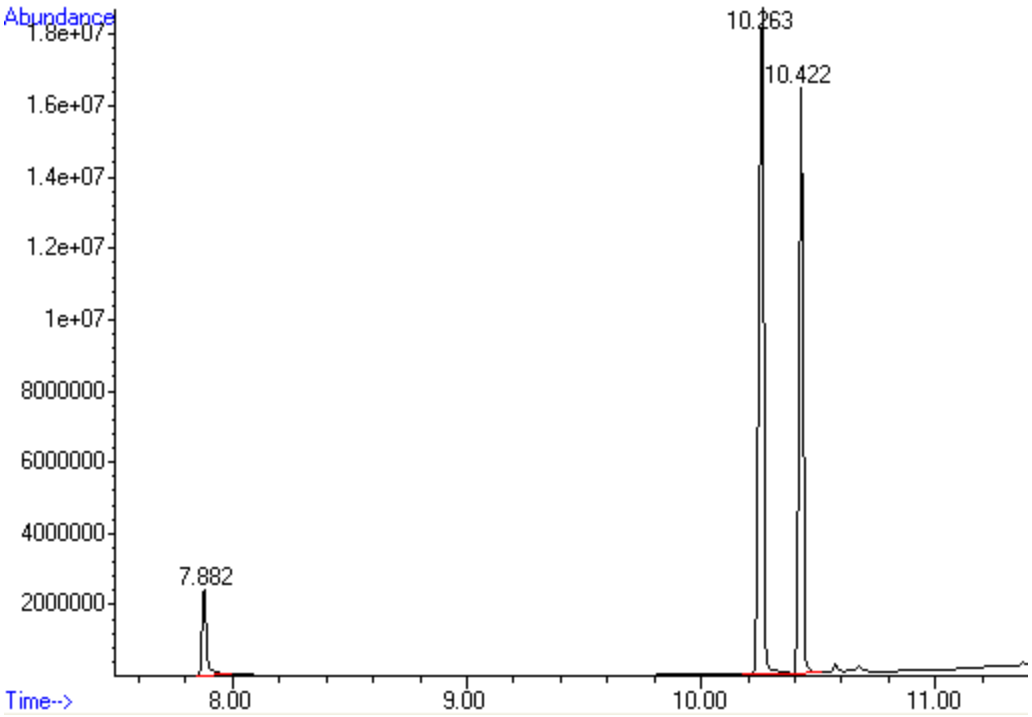

Figure S41: GC-MS spectrum demonstrating arene formation by complex **2** in C_7D_8 at 80 °C. The peak at 7.882 corresponds to 1,3,5-trimethoxybenzene, the peak at 10.263 corresponds to the 1,2,4-isomer, and the peak at 10.422 corresponds to the 1,3,5-isomer.

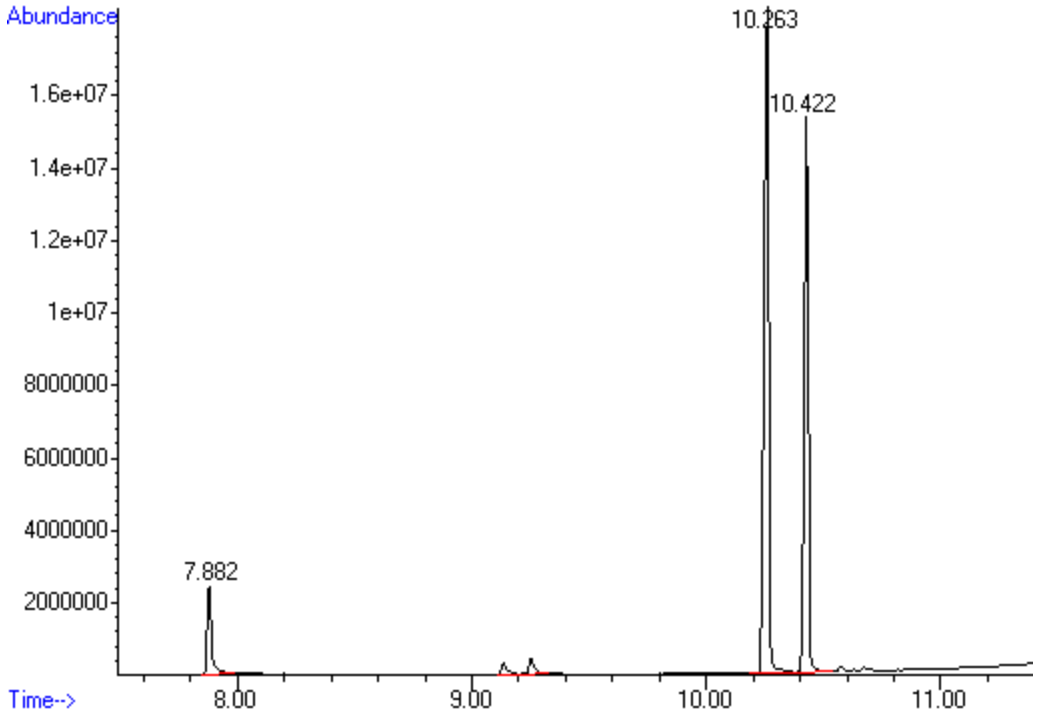

Figure S42: GC-MS spectrum demonstrating arene formation by complex **4** in C_7D_8 at 80 °C. The peak at 7.882 corresponds to 1,3,5-trimethoxybenzene, the peak at 10.263 corresponds to the 1,2,4-isomer, and the peak at 10.422 corresponds to the 1,3,5-isomer.

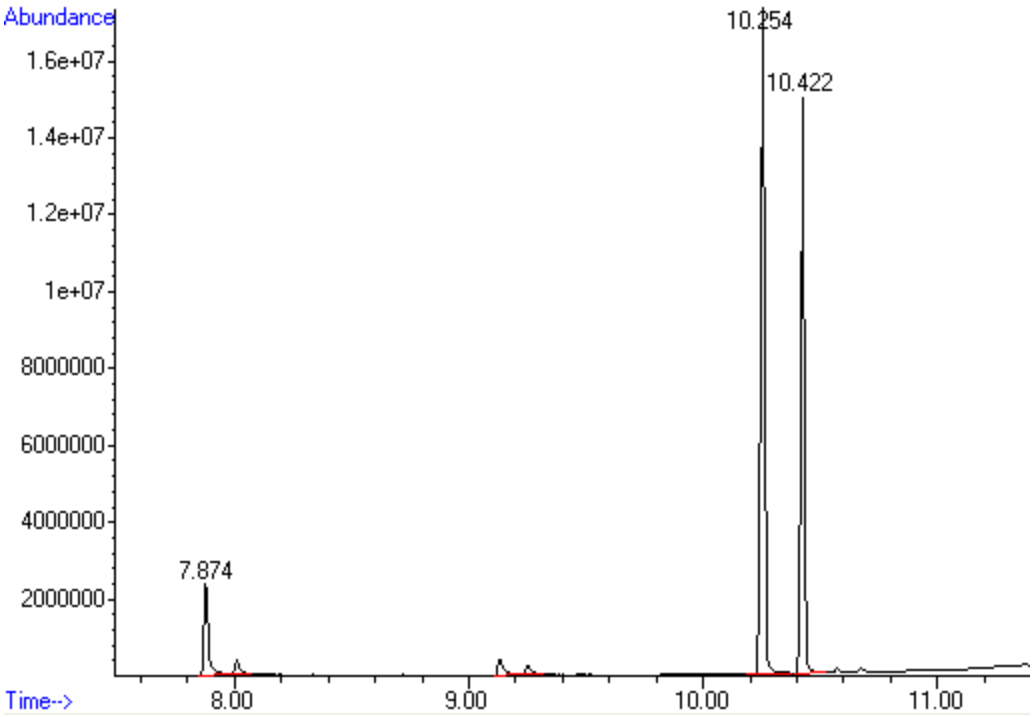

Figure S43: GC-MS spectrum demonstrating arene formation by complex **5** in C_7D_8 at 80 °C. The peak at 7.874 corresponds to 1,3,5-trimethoxybenzene, the peak at 10.254 corresponds to the 1,2,4-isomer, and the peak at 10.422 corresponds to the 1,3,5-isomer.

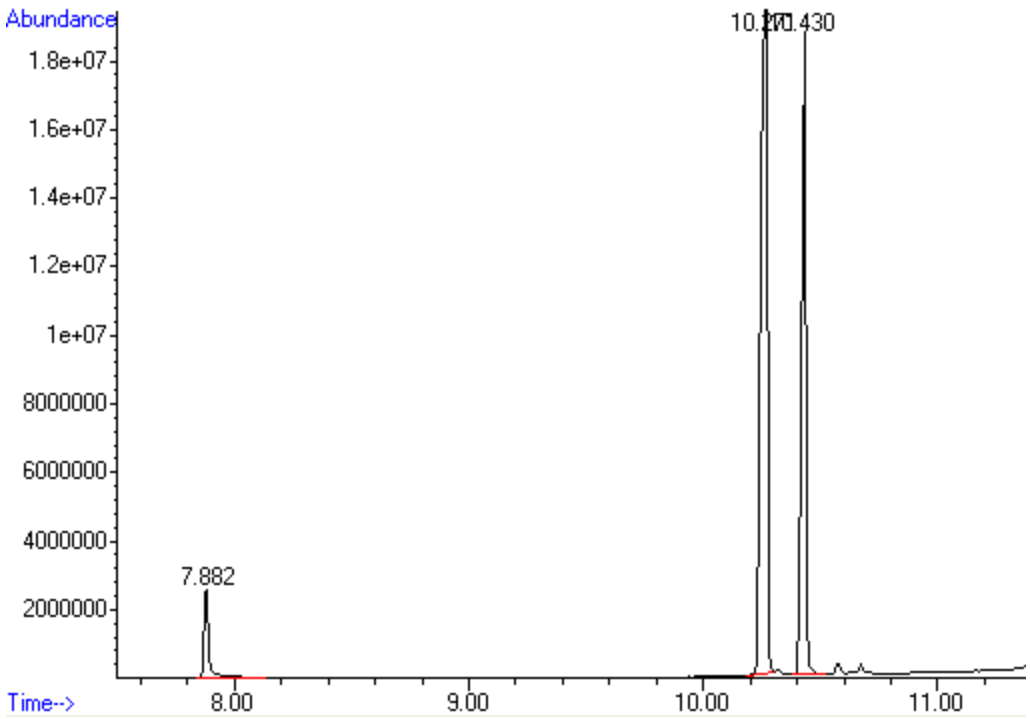

Figure S44: GC-MS spectrum demonstrating arene formation by $Co_2(CO)_8$ in C_7D_8 at 80 °C. The peak at 7.882 corresponds to 1,3,5-trimethoxybenzene, the peak at 10.271 corresponds to the 1,2,4-isomer, and the peak at 10.430 corresponds to the 1,3,5-isomer.

8. Computational Details

All density functional theory calculations were performed in Gaussian 09 revision D01.[2] The B3LYP functional was employed in combination with the semi-empirical D3 dispersion correction developed by Grimme and co-workers, including the Becke-Johnson damping, in combination with the 6-31G(d) basis set.[3] Because the spin states were known experimentally in most cases (except **3**), only the experimental spin state was explored but multiple guess wavefunctions (including broken symmetry options) were used as initial guesses. In all cases the results converged to a single wavefunction that was confirmed to be stable.[4] All structures were confirmed to be minima by analyzing the harmonic frequencies.[5]

All topological analyses were performed using Multiwfn version 3.5.[6] The source function analyses were performed with the bond critical point between the Co centers used as the reference point. Integration of the source function used atomic-center and uniform grids (high quality, 0.06 Bohr spacing) with exact refinement of the basin boundaries (option 2). As Tables S4-S5 demonstrate, we observe small negative contributions to the source function from the cobalt centers and major contributions from the carbonyls for the two isomers of $Co_2(CO)_8$ similar to what Gatti and Lasi reported.[7] One small difference is that the contributions from the Co centers in the bridged isomer are small and negative vs. small and positive, though it should be noted that we identified a bcp for the bridged isomer and evaluated the source function at that point rather than the midpoint of the Co-Co separation as they did. Looking at Table S6 for **i** and Table S7 for **iib**, the story is generally the same: (i) most of the Co centers make negative contributions (all are small), (ii) the carbonyls are the primary contributors, and (iii) **i** has larger contributions from Co to the source function than **iib**, consistent with all other indicators of less bonding in the bridged species. The primary difference compared to $Co_2(CO)_8$ is unequal contributions from the two Co centers. For both species, the Co bound to the bis(imino)pyridine makes a much smaller contribution (-0.82% vs. -12% and +2.9% vs. -1.9%) which further reinforces the assignment of different oxidation states for the two Co centers.

Figure S45. Spin density isosurface plot (iso = 0.002 au) for species **v**.

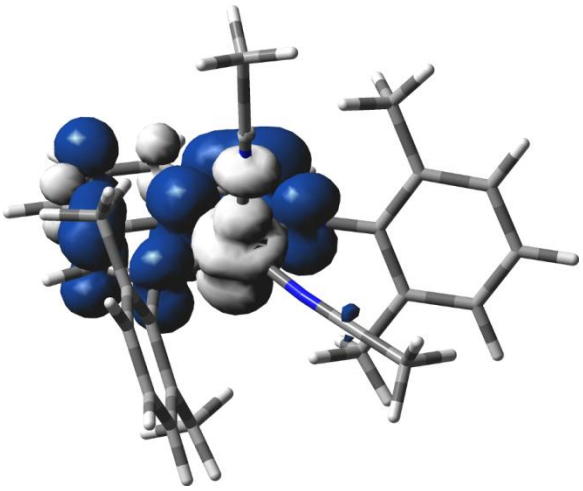

Table S2. Comparison of select bond lengths (Å) in **i** and **1**. See Figure 1 in manuscript for atom labels.

Bond	i	1
Co1---Co2	2.691	2.798
Co2-N1	1.925	1.920
Co2-N2	1.938	1.924
Co2-N3	1.831	1.833
N_{im}-C_{im}	1.319	1.32*
C_{im}-C_{py}	1.427	1.43*
C_{py}-N_{py}	1.367	1.372*
Co2-C5	1.760	1.774
Co1-C1	1.772	1.773
Co1-C2	1.755	1.754
Co1-C3	1.757	1.778
Co1-C4	1.769	1.784

im = iminopyridine, py = pyridine; *values in two arms averaged

Table S3. Comparison of select bond lengths (Å) in **iib** and **2b**. See Figure 3 in manuscript for atom labels.

Bond	iia	2a
Co3---Co4	2.568	2.594
Co3-N1	1.948	1.985
Co3-N2	1.932	1.954
Co3-N3	1.826	1.867
N_{im}-C_{im}	1.32*	1.307
C_{im}-C_{py}	1.42*	1.43*
C_{py}-N_{py}	1.373	1.36*
Co3-C6	1.876	1.960
Co3-C6	1.915	1.894
Co4-C7	1.832	1.814
Co4-C7	2.077	2.220
Co4-C8	1.788	1.796
Co4-C9	1.790	1.802
Co4-C10	1.766	1.750

im = iminopyridine, py = pyridine; *values in two arms averaged

Figure S46. Plot of bond critical point locations for unbridged $Co_2(CO)_8$. Yellow spheres correspond to (3,+1) bcps and orange spheres correspond to (3,–1) bcps.

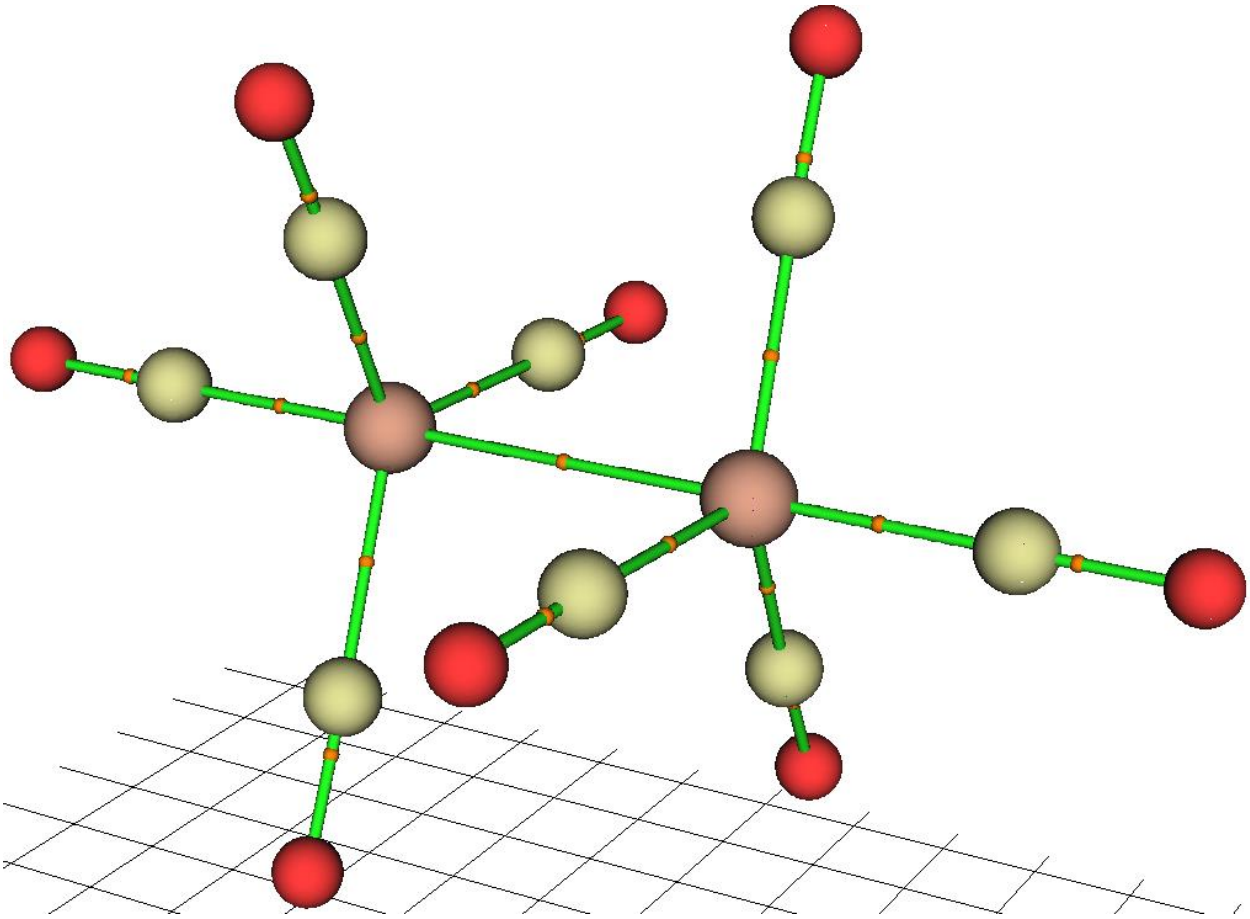

Figure S47. Plot of bond critical point locations for bridged $Co_2(CO)_8$. Yellow spheres correspond to (3,+1) bcps and orange spheres correspond to (3,–1) bcps.

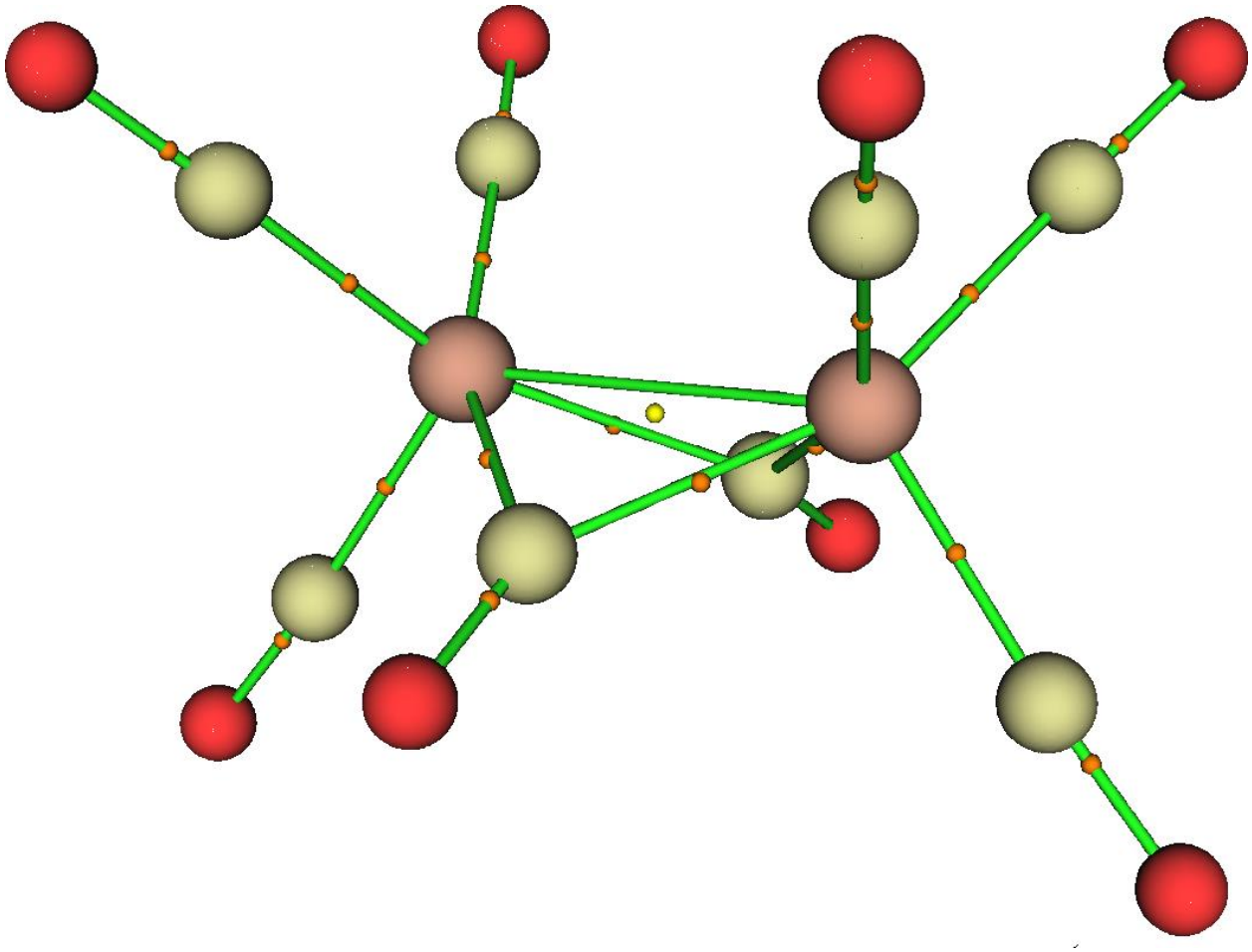

Figure S48. Plot of bond critical point locations for **i**. Yellow spheres correspond to (3,+1) bcps and orange spheres correspond to (3,–1) bcps.

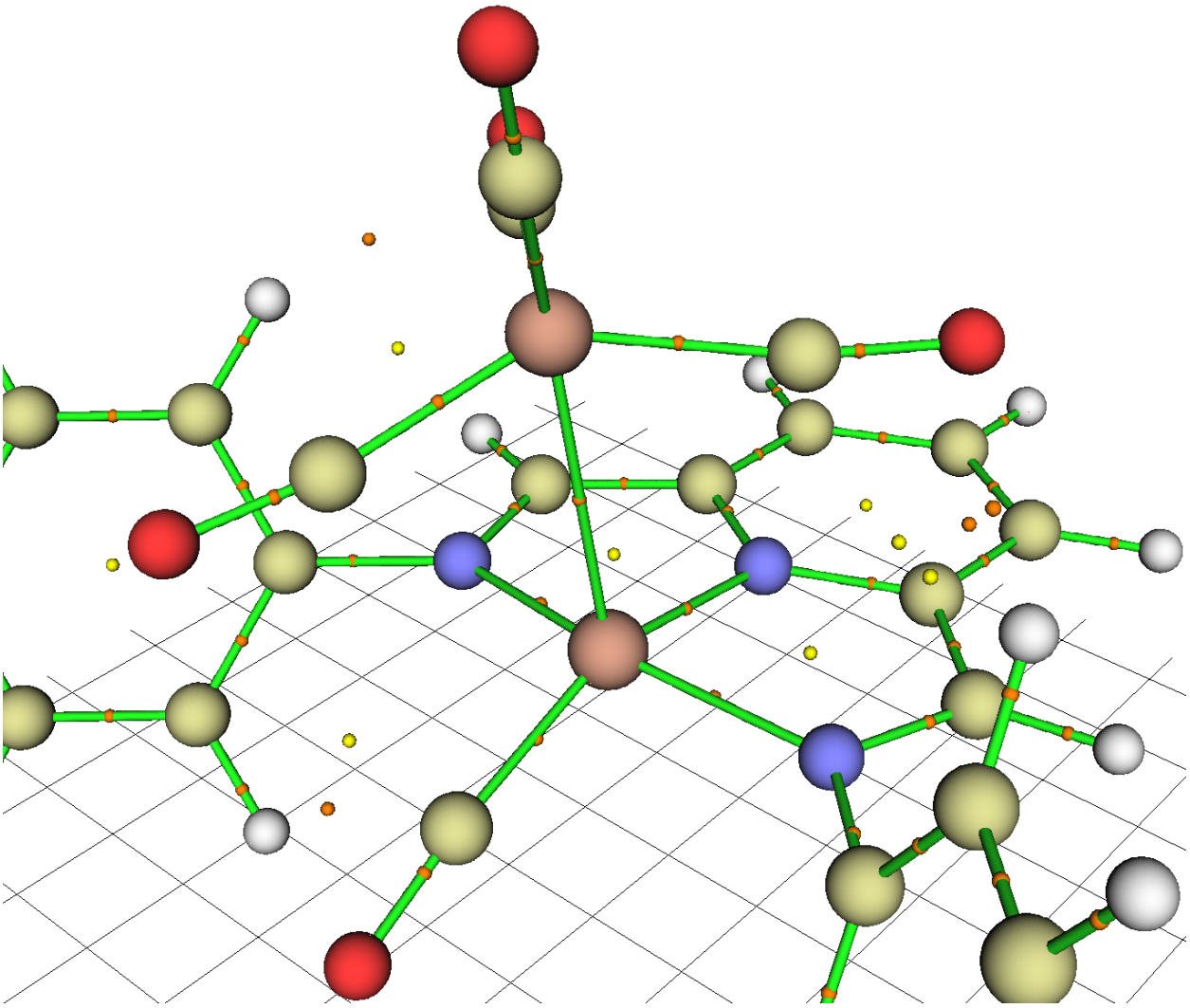

Figure S49. Plot of bond critical point locations for **iib**. Yellow spheres correspond to (3,+1) bcps and orange spheres correspond to (3,–1) bcps.

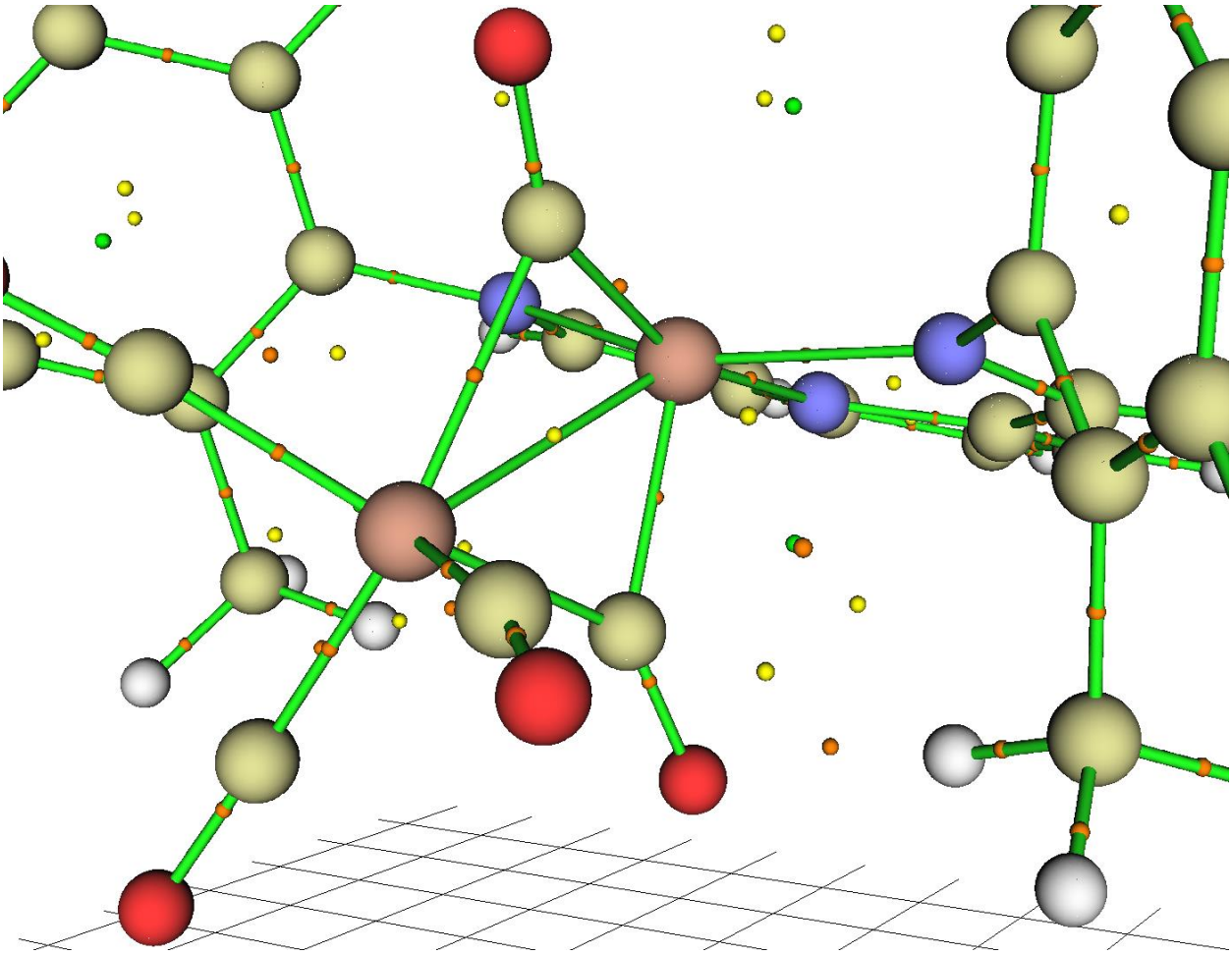

Figure S50. Schematic representation of all computed model structures.

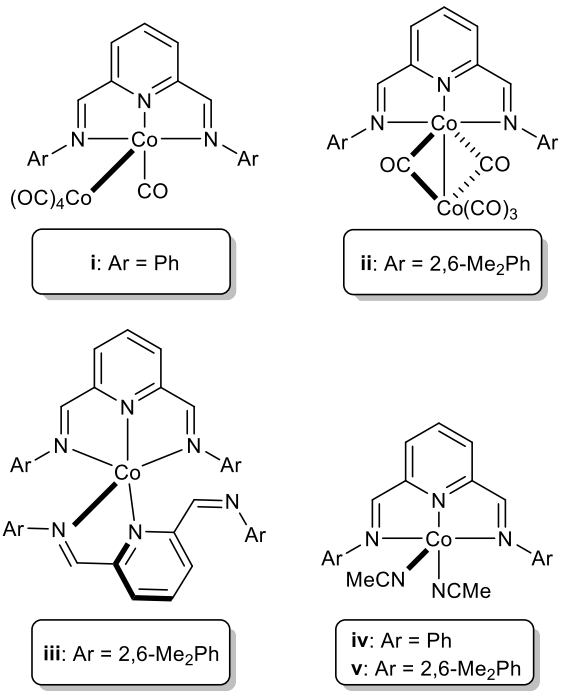

Table S4. Source function analysis for the (3,–1) bcp between the Co centers in Figure S46. The atom ordering is the same as reported in Table S8.

Basin	% Contribution
Co	-1.71
Co	-1.71
C	1.63
O	12.63
C	1.59
O	12.66
C	1.68
O	12.62
C	1.57
O	7.34
C	1.62
O	12.64
C	1.69
O	12.62
C	1.59
O	12.66
C	1.56
O	7.34

Table S5. Source function analysis for the (3,+1) bcp between the Co centers in Figure S47. The atom ordering is the same as reported in Table S8.

Basin	% Contribution
Co	-0.15
Co	-0.17
C	1.65
O	20.11
C	1.67
O	7.78
C	1.65
O	7.79
C	1.85
O	7.54
C	1.65
O	7.80
C	1.93
O	20.14
C	1.63
O	7.76
C	1.82
O	7.55

Table S6. Source function analysis for the (3,–1) bcp between the Co centers in Figure S48. The atom ordering is the same as reported in Table S8.

Basin	% Contribution
Co	-0.82
N	-2.10
C	1.55
C	1.90
C	2.04
C	1.88
C	1.27
H	1.56
H	1.55
H	1.57
C	4.09
H	3.12
C	3.91
H	2.84
N	-4.47
N	-3.20
Co	-11.94
C	2.01
O	12.52
C	3.35
O	9.44
C	1.39
O	19.19
C	2.08
O	17.67
C	3.00
O	12.97
C	-1.17
C	-0.09
C	0.36
C	1.13
H	-0.06
C	1.16
H	0.61
C	1.02
H	1.17
H	1.15
H	1.14
C	-1.14
C	0.51
C	-0.57
C	1.04
H	0.55
C	1.04
H	-0.39

C	0.90
H	1.10
H	1.06
H	1.14

Table S7. Source function analysis for the (3,+1) bcp between the Co centers in Figure S49. The atom ordering is the same as reported in Table S8.

Basin	% Contribution
C	0.84
C	1.15
C	1.25
C	1.38
C	1.15
H	0.91
H	0.88
H	0.87
N	0.12
C	2.92
C	2.87
N	-2.63
N	-2.54
Co	2.89
C	-1.98
C	-0.34
C	-0.88
C	0.78
C	0.76
C	0.69
H	1.04
H	1.04
C	-1.64
C	-0.78
C	-0.22
C	0.70
C	0.73
C	0.67
H	0.94
H	0.95
C	0.83
C	-0.06
O	21.97
O	22.31
Co	-1.88
C	1.94
C	2.46
C	1.81
O	9.01
O	8.37
O	9.45
H	1.84
H	1.85
C	-0.04
H	0.62

H	1.54
H	-0.95
C	0.10
H	1.29
H	1.64
H	-2.21
C	0.20
H	1.30
H	1.01
H	-1.53
C	0.08
H	1.55
H	1.20
H	-2.19
H	0.95
H	1.02

Table S8. Cartesian coordinates (Å) for all optimized structures.

```
-----
i S=0
-----
Co  0.099794   0.101661  -0.752323
N   0.143717   1.923311  -0.936113
C  -1.030555   2.621815  -0.971129
C   1.349028   2.562658  -1.015539
C  -1.019709   4.014112  -1.030736
C   1.403478   3.953946  -1.083057
C   0.209380   4.680936  -1.078226
H  -1.955012   4.563919  -1.044984
H   2.363489   4.456693  -1.136697
H   0.235402   5.764420  -1.122670
C  -2.130325   1.712433  -0.979429
H  -3.168536   2.028729  -1.014076
C   2.402565   1.599880  -1.005542
H   3.456608   1.858367  -1.036003
N  -1.797933   0.436296  -0.959392
N   2.001382   0.346310  -0.923672
Co -0.184017  -0.107547   1.915070
C   0.120950  -1.546393  -1.368585
O   0.165016  -2.578119  -1.881276
C   0.306962  -0.810422   3.448914
O   0.599217  -1.233257   4.482597
C  -0.837309  -1.607208   1.232692
O  -1.330469  -2.623212   0.975585
C   1.160063   1.007616   1.746799
O   2.000520   1.808803   1.813310
C  -1.531446   1.026064   2.078898
O  -2.363376   1.828840   2.156607
C  -2.866695  -0.511596  -0.947109
C  -3.858849  -0.449251   0.037988
C  -2.912364  -1.510967  -1.922829
C  -4.879039  -1.398452   0.053392
H  -3.806625   0.315920   0.802948
C  -3.939642  -2.450894  -1.904240
H  -2.153563  -1.538789  -2.695271
C  -4.922002  -2.402610  -0.913820
H  -5.635111  -1.356479   0.831871
H  -3.969460  -3.223907  -2.666235
H  -5.714176  -3.145031  -0.895105
C   3.015624  -0.656798  -0.811950
C   3.195289  -1.583275  -1.842071
C   3.817228  -0.711422   0.333121
C   4.175290  -2.566806  -1.722866
H   2.575491  -1.522007  -2.729476
C   4.790646  -1.703361   0.446206
H   3.658394   0.007506   1.128231
C   4.971939  -2.632831  -0.578464
H   4.314474  -3.282823  -2.527383
H   5.403646  -1.750239   1.341477
H   5.728526  -3.406260  -0.485623

-----
iib S=0
-----
C   0.595066   5.213772  -0.709994
C   1.723764   4.384520  -0.700169
C   1.564501   3.022723  -0.459113
C  -0.793127   3.306340  -0.213566
C  -0.667110   4.676772  -0.444693
H   0.705714   6.277997  -0.888059
H   2.717557   4.792864  -0.853726
H  -1.545241   5.313144  -0.399008
N   0.311253   2.493171  -0.284603
C  -1.928853   2.546849   0.165097
C   2.552343   2.022107  -0.240611
N   2.076469   0.858323   0.163731
N  -1.667782   1.279528   0.460736
Co  0.136229   0.710217   0.066710
C  -2.786772   0.443523   0.775412
C  -2.953744   0.019743   2.105955
C  -3.672550   0.052423  -0.246341
C  -4.006639  -0.854845   2.389290
C  -4.703392  -0.833660   0.081915
C  -4.866471  -1.293762   1.385574
H  -4.147598  -1.192677   3.412353
H  -5.380417  -1.164682  -0.701116
C   3.022927  -0.157504   0.521167
C   3.698418  -0.897766  -0.462477
C   3.233923  -0.380683   1.896150
C   4.552091  -1.923551  -0.038119
C   4.099861  -1.408084   2.272270
C   4.745908  -2.186814   1.313154
H   5.060860  -2.522821  -0.788094
H   4.264943  -1.596664   3.329519
C   0.122043   0.068272  -1.696448
C   0.111590  -0.888140   0.962468
O   0.332443   0.567788  -2.743997
O   0.278253  -1.464275   1.971301
Co -0.413294  -1.597480  -0.917288
C  -1.560903  -2.570198   0.052871
C  -1.404045  -1.799693  -2.365420
C   1.030063  -2.626658  -1.154400
O  -2.280055  -3.281078   0.600956
O  -2.035102  -2.020721  -3.304786
O   1.824038  -3.420077  -1.414803
H  -2.936202   2.948214   0.222491
H   3.620275   2.198415  -0.334945
C  -2.055641   0.522044   3.209509
H  -1.857078   1.593531   3.107030
H  -2.521066   0.349734   4.184568
H  -1.088187   0.011738   3.206817
C  -3.549469   0.577253  -1.656403
H  -3.989401  -0.126101  -2.368390
H  -4.077832   1.532710  -1.770106
H  -2.511463   0.748257  -1.947894
C   2.591264   0.506120   2.931854
H   2.747622   0.103001   3.936123
H   3.020888   1.516014   2.902127
H   1.517388   0.613472   2.765045
C   3.560584  -0.600897  -1.935529
H   4.286060   0.160964  -2.250345
H   3.755371  -1.500807  -2.525348
H   2.571821  -0.228821  -2.200197
H   5.403952  -2.994269   1.621037
H  -5.667214  -1.988587   1.620904

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iii S=1
-----
Co  0.540156   0.012262   0.409668
N  -0.023921  -0.497952   2.181280
C   0.123597  -1.816331   2.536841
C  -0.531063   0.393146   3.086067
C  -0.265082  -2.266058   3.803838
C  -0.928246  -0.010401   4.353938
C  -0.797473  -1.361814   4.719697
H  -0.147903  -3.314742   4.059634
H  -1.332481   0.717466   5.050563
H  -1.102568  -1.693452   5.705799
N  -0.351776   0.774047  -1.294847
C  -1.659547   0.759245  -1.609731
C   0.468786   1.663387  -1.905700
C  -2.195241   1.669932  -2.533966
C   0.004315   2.587837  -2.836775
```

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C  -1.359079   2.596029  -3.140807
H  -3.255865   1.617402  -2.747149
H   0.689963   3.292846  -3.293440
H  -1.756426   3.314057  -3.850351
C   0.714342  -2.613149   1.507530
H   0.940532  -3.664993   1.675721
C  -0.652957   1.745899   2.587066
H  -1.158952   2.492862   3.202526
C   1.871584   1.548716  -1.525295
H   2.621178   2.112667  -2.079470
C  -2.481854  -0.268713  -0.956734
H  -1.927826  -1.008437  -0.376045
N   1.003594  -2.018927   0.368153
N   2.187384   0.767676  -0.548047
N  -3.748132  -0.276934  -1.129417
N  -0.198315   2.026757   1.404519
C  -0.507555   3.272015   0.788819
C   0.533392   4.174634   0.475404
C  -1.839840   3.543861   0.405578
C   0.227080   5.313417  -0.272522
C  -2.093259   4.689149  -0.357579
C  -1.072101   5.564600  -0.709303
H   1.021569   6.018359  -0.501682
H  -3.114574   4.892846  -0.668102
H  -1.289322   6.450884  -1.297706
C   1.780836  -2.712962  -0.605920
C   3.114869  -3.068162  -0.316199
C   1.220201  -2.968000  -1.874424
C   3.880547  -3.654710  -1.330413
C   2.015722  -3.574404  -2.848930
C   3.343219  -3.908501  -2.587699
H   4.913843  -3.915275  -1.118348
H   1.582239  -3.790221  -3.821597
H   3.951132  -4.372301  -3.358635
C   3.558029   0.490012  -0.272676
C   4.029081   0.604146   1.052505
C   4.395818   0.031759  -1.316678
C   5.384770   0.364707   1.290810
C   5.734163  -0.232217  -1.014503
C   6.237685  -0.042211   0.269192
H   5.765557   0.481127   2.301497
H   6.384390  -0.598461  -1.803573
H   7.285890  -0.233388   0.477555
C  -4.620795  -1.212290  -0.563818
C  -5.765647  -1.494449  -1.353710
C  -4.462425  -1.807011   0.715807
C  -6.704806  -2.409949  -0.883635
C  -5.449887  -2.692928   1.154772
C  -6.551417  -3.009959   0.364472
H  -7.571269  -2.642009  -1.495914
H  -5.349660  -3.138617   2.140770
H  -7.298236  -3.708569   0.729387
C   3.134943   0.914123   2.229033
H   2.243285   1.475735   1.962050
H   2.801295  -0.015556   2.707575
H   3.682178   1.487407   2.983615
C   3.890107  -0.268264  -2.709815
H   2.870799  -0.664241  -2.696152
H   3.907179   0.609557  -3.366623
H   4.523114  -1.028937  -3.171990
C   1.935833   3.979735   0.994920
H   1.940837   3.812905   2.077184
H   2.439763   3.123713   0.540743
H   2.542448   4.866599   0.792861
C  -2.996301   2.658496   0.802986
H  -2.703714   1.614497   0.916302
H  -3.430024   2.979034   1.758563
H  -3.794034   2.698371   0.056230
C  -3.320813  -1.495360   1.654097
H  -2.425443  -2.088512   1.435529
H  -3.024032  -0.443231   1.618118
H  -3.608483  -1.723771   2.684200
C  -5.944618  -0.836378  -2.697446
H  -5.839808   0.250518  -2.618664
H  -5.189870  -1.175343  -3.416782
H  -6.930447  -1.065021  -3.111254
C   3.740666  -2.839893   1.037733
H   3.339135  -1.955047   1.533054
H   3.575974  -3.694229   1.706358
H   4.820416  -2.704535   0.938804
C  -0.217933  -2.632812  -2.176438
H  -0.885700  -2.947174  -1.367829
H  -0.357834  -1.556048  -2.313061
H  -0.544173  -3.128001  -3.095104

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iii S=0
-----
Co  0.482201   0.161399   0.579683
N  -0.433458  -0.056474   2.158515
C  -0.864734  -1.314134   2.506651
C  -0.657793   1.023352   2.976109
C  -1.562060  -1.509616   3.696055
C  -1.334595   0.858068   4.184093
C  -1.794291  -0.414943   4.540318
H  -1.911240  -2.501512   3.964015
H  -1.505359   1.712097   4.831499
H  -2.329016  -0.555901   5.472878
N  -0.184543   0.784491  -1.252270
C  -1.443578   0.940476  -1.689633
C   0.835325   1.311892  -1.970410
C  -1.727116   1.657595  -2.862737
C   0.628139   2.050117  -3.132102
C  -0.683699   2.228429  -3.578384
H  -2.761135   1.739078  -3.175880
H   1.471303   2.473687  -3.666190
H  -0.882208   2.798449  -4.480147
C  -0.439205  -2.262752   1.529174
H  -0.625195  -3.329828   1.617569
C  -0.160251   2.214105   2.370726
H  -0.315717   3.200399   2.800615
C   2.153207   0.960716  -1.461445
H   3.037851   1.253618  -2.021974
C  -2.496255   0.276590  -0.906174
H  -2.161174  -0.206353   0.014812
N   0.264591  -1.769125   0.524764
N   2.223743   0.250449  -0.383015
N  -3.693954   0.216587  -1.341567
N   0.440637   2.059272   1.203789
C   0.670975   3.225326   0.401243
C   1.980163   3.686729   0.153201
C  -0.443242   3.854904  -0.196999
C   2.158739   4.704467  -0.790547
C  -0.214595   4.862320  -1.138778
C   1.076952   5.270554  -1.458188
H   3.164691   5.067605  -0.982034
H  -1.067956   5.334883  -1.617242
H   1.237090   6.053376  -2.193368
C   0.903154  -2.713001  -0.353187
C   2.033192  -3.407369   0.126472
C   0.407776  -2.939714  -1.651845
C   2.701365  -4.274373  -0.743869
C   1.096951  -3.831979  -2.479590
C   2.246681  -4.482806  -2.041620
H   3.583379  -4.796893  -0.384668
H   0.710835  -4.024089  -3.476976
H   2.771420  -5.167145  -2.701528
C   3.469025  -0.358986  -0.036150
C   3.931499  -0.328582   1.299238
C   4.199354  -1.049760  -1.039657
C   5.173172  -0.903804   1.585501
C   5.417852  -1.634049  -0.688688
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C   5.920758  -1.545504   0.605880
H   5.542234  -0.857001   2.606405
H   5.972974  -2.175502  -1.449053
H   6.878394  -1.993460   0.852737
C  -4.685646  -0.486145  -0.629549
C  -5.478940  -1.362407  -1.405222
C  -4.926146  -0.312676   0.753166
C  -6.475344  -2.103534  -0.770994
C  -5.955484  -1.057139   1.337453
C  -6.715092  -1.956530   0.594039
H  -7.076524  -2.791957  -1.358239
H  -6.167521  -0.915894   2.393996
H  -7.506428  -2.525433   1.072691
C   3.166097   0.264048   2.457668
H   2.257676   0.769622   2.149069
H   2.884282  -0.526085   3.163877
H   3.789137   0.977685   3.006447
C   3.699452  -1.265373  -2.451060
H   2.610324  -1.332565  -2.499307
H   4.024846  -0.476397  -3.139610
H   4.094706  -2.208900  -2.834007
C   3.169605   3.190360   0.934277
H   2.923739   3.069580   1.992154
H   3.541845   2.226625   0.580107
H   3.991989   3.907029   0.859680
C  -1.864836   3.508750   0.172419
H  -1.979872   2.468290   0.472727
H  -2.208730   4.124037   1.013763
H  -2.542093   3.698316  -0.664799
C  -4.172967   0.687513   1.599695
H  -3.224579   0.291446   1.976515
H  -3.948344   1.601040   1.041749
H  -4.771465   0.966848   2.471608
C  -5.212711  -1.519424  -2.879959
H  -5.135978  -0.543692  -3.370707
H  -4.263801  -2.039060  -3.064362
H  -6.008745  -2.095245  -3.359786
C   2.510596  -3.290375   1.552517
H   2.249024  -2.333214   2.001313
H   2.065731  -4.077262   2.175389
H   3.595930  -3.405111   1.603612
C  -0.865315  -2.310798  -2.156848
H  -1.558623  -2.088922  -1.344045
H  -0.673060  -1.377014  -2.694036
H  -1.369980  -2.986657  -2.853779

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iv S=0
-----
Co  0.026163   0.283897  -0.234859
N   0.122619   2.093169  -0.514898
C   1.353707   2.687126  -0.557978
C  -1.034981   2.822210  -0.517803
C   1.450311   4.074360  -0.653049
C  -0.976409   4.212642  -0.611234
C   0.274951   4.836306  -0.681090
H   2.423564   4.551342  -0.703303
H  -1.890609   4.796793  -0.628715
H   0.335062   5.916303  -0.757725
C   2.380881   1.694044  -0.517935
H   3.440977   1.929948  -0.559394
C  -2.164932   1.951240  -0.446529
H  -3.193236   2.302833  -0.455649
N   1.951284   0.444899  -0.461047
N  -1.873961   0.661163  -0.405896
N   0.072184   0.133629   1.759025
C   0.128711   0.135403   2.914001
N  -0.128657  -1.585064  -0.459898
C  -0.331951  -2.717122  -0.565874
C   0.200909   0.131893   4.369032
H  -0.692367  -0.341929   4.787384
H   1.084313  -0.423895   4.697984
H   0.266963   1.157905   4.743764
C  -0.638227  -4.129872  -0.715249
H  -0.253280  -4.694999   0.138991
H  -1.725347  -4.251904  -0.766911
H  -0.187703  -4.521529  -1.632564
C  -2.935916  -0.274980  -0.273137
C  -3.125386  -1.249301  -1.260277
C  -3.769351  -0.246753   0.850012
C  -4.147461  -2.186324  -1.121669
H  -2.486029  -1.243740  -2.137008
C  -4.786265  -1.192297   0.985598
H  -3.603919   0.506337   1.614848
C  -4.976812  -2.164592   0.003430
H  -4.309696  -2.923766  -1.902763
H  -5.429878  -1.167285   1.859729
H  -5.771880  -2.896159   0.108049
C   2.906744  -0.598984  -0.337171
C   2.893314  -1.659005  -1.250965
C   3.847683  -0.581384   0.699437
C   3.824907  -2.687209  -1.131795
H   2.172637  -1.648123  -2.061472
C   4.771916  -1.618925   0.817095
H   3.836711   0.236263   1.414245
C   4.763899  -2.672999  -0.097029
H   3.826535  -3.496964  -1.855516
H   5.498159  -1.602484   1.624135
H   5.486888  -3.477614  -0.006847

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v S=0
-----
Co -0.026556   0.370483  -0.055958
N  -0.123231   2.121651  -0.588495
C  -1.353746   2.680755  -0.802492
C   1.033676   2.846016  -0.695856
C  -1.452743   4.032290  -1.124246
C   0.970850   4.201863  -1.015704
C  -0.280503   4.794638  -1.222654
H  -2.424167   4.480790  -1.304501
H   1.882857   4.782010  -1.110993
H  -0.342565   5.847155  -1.475980
C  -2.370927   1.676828  -0.704968
H  -3.425978   1.877086  -0.873202
C   2.165704   1.991120  -0.510494
H   3.193796   2.329801  -0.609134
N  -1.930168   0.464719  -0.433135
N   1.871010   0.727761  -0.263836
N   0.173498  -1.512046  -0.061799
C   0.454020  -2.631860  -0.096388
N  -0.195175   0.425950   1.939372
C  -0.363050   0.511182   3.080565
C   0.868060  -4.022487  -0.173337
H   1.953047  -4.054668  -0.319806
H   0.611250  -4.550400   0.749867
H   0.373331  -4.516491  -1.015245
C  -0.589387   0.615124   4.515045
H  -1.661775   0.551251   4.724745
H  -0.075749  -0.198274   5.036480
H  -0.210420   1.571767   4.887398
C   2.918617  -0.237945  -0.144666
C   3.622593  -0.369300   1.064024
C   3.159561  -1.087946  -1.240206
C   4.566738  -1.396874   1.167996
C   4.112287  -2.101065  -1.094101
C   4.808058  -2.262331   0.103841
H   5.118838  -1.512003   2.096573
H   4.318658  -2.756438  -1.936274
H   5.546121  -3.052612   0.202422
C  -2.851583  -0.622693  -0.331443
C  -3.695488  -0.737320   0.787185
```

```
C  -2.843898  -1.589304  -1.356170
C  -4.515034  -1.868597   0.879638
C  -3.682108  -2.698124  -1.224868
C  -4.507785  -2.845289  -0.111138
H  -5.168132  -1.975212   1.741585
H  -3.693831  -3.446786  -2.012321
H  -5.150459  -3.715774  -0.021379
C  -3.762435   0.326472   1.856918
H  -2.811576   0.848004   1.978632
H  -4.517957   1.085199   1.615839
H  -4.049338  -0.112947   2.817579
C  -2.005148  -1.399258  -2.594849
H  -2.411056  -0.598162  -3.225230
H  -0.978468  -1.113875  -2.351374
H  -1.982987  -2.312782  -3.195495
C   3.386224   0.576337   2.215285
H   3.810038   1.567974   2.014275
H   2.319514   0.719314   2.404563
H   3.856610   0.199207   3.127471
C   2.431122  -0.890558  -2.545530
H   1.347702  -0.840218  -2.399264
H   2.724358   0.050511  -3.026137
H   2.651754  -1.702776  -3.243295

-----
unbridged Co2(CO)8
-----
Co -1.320629  -0.000367   0.000099
Co  1.320621   0.000359  -0.000086
C  -1.155710  -0.870402  -1.559917
O  -1.082264  -1.429445  -2.561636
C   1.156369   0.919015  -1.532080
O   1.083112   1.509540  -2.515578
C  -1.155726   1.785653   0.028195
O  -1.083190   2.932739   0.046070
C   3.083963  -0.000979   0.000334
O   4.230766  -0.002122   0.000846
C   1.155711   0.870323   1.559960
O   1.082631   1.429619   2.561563
C   1.155724  -1.785661  -0.028105
O   1.083207  -2.932740  -0.046393
C  -1.156397  -0.918993   1.532098
O  -1.083435  -1.509632   2.515548
C  -3.083970   0.000985  -0.000378
O  -4.230773   0.002112  -0.000547

-----
bridged Co2(CO)8
-----
Co  1.255352  -0.002743   0.002935
Co -1.255338   0.002334   0.003274
C  -0.003344  -1.297381  -0.676045
O  -0.005306  -2.343448  -1.205446
C  -1.884778  -1.301578   1.083762
O  -2.317967  -2.123659   1.754608
C   1.872718  -1.305898   1.091348
O   2.296310  -2.127153   1.769337
C  -2.318576  -0.001793  -1.443305
O  -3.068804  -0.004367  -2.310397
C  -1.863139   1.321862   1.077368
O  -2.278695   2.154277   1.746702
C   0.002979   1.284545  -0.698923
O   0.004852   2.320853  -1.247267
C   1.874567   1.316923   1.070162
O   2.298501   2.149414   1.734116
C   2.319456  -0.016672  -1.442904
O   3.071149  -0.024542  -2.308708
```

Table S9. Frequencies (cm^{-1}) for all optimized structures. Some small (< 10 cm^{-1}) imaginary frequencies corresponding to breathing motions were ignored.

---
i S=0

10.7498	21.6465	23.6173
34.8526	47.2050	52.5003
58.7676	65.1113	71.5491
80.2367	90.0683	97.1271
99.7425	107.7153	113.5465
125.2558	137.3234	146.6721
158.9062	187.4721	189.7537
207.2773	209.9958	236.7945
253.3842	269.5767	302.6724
325.8770	340.6824	350.4969
354.8451	379.8190	389.3906
421.4720	425.0470	430.1244
443.6784	449.7950	470.9494
480.3334	497.1534	504.7633
513.3335	522.7326	527.0560
529.1519	553.4961	557.6565
563.8072	569.1997	576.8657
583.6752	592.4548	598.4086
610.3712	623.4934	624.7797
638.5320	639.2461	684.2258
693.2402	713.9073	715.8661
720.1014	775.7409	785.9568
788.0447	818.6396	853.1239
855.3336	869.8433	881.6908
894.3447	921.1888	924.4834
936.7735	947.3526	971.3231
971.4983	972.3368	996.2606
996.8624	1022.6557	1023.0488
1058.2620	1060.0947	1061.2178
1102.8260	1106.2207	1115.6200
1119.3482	1193.8779	1194.4859
1202.5226	1210.5432	1214.1231
1237.4619	1249.1317	1257.1260
1281.1095	1333.6296	1342.8720
1351.0151	1365.8825	1369.7448
1395.1626	1402.0129	1422.1569
1480.9106	1499.2153	1501.0406
1521.7658	1541.1553	1544.9757
1550.8842	1594.8224	1644.3654
1645.0100	1657.0632	1659.7248
1672.3056	2009.4271	2034.7378
2050.7217	2089.0450	2119.3720
3192.0121	3193.2182	3202.1905
3203.4496	3207.9193	3209.9972
3210.9304	3213.8666	3215.7667
3219.6422	3227.1345	3230.3012
3237.1341	3239.1961	3242.7188

---
iib S=0

14.9671	31.4686	38.2635
43.8557	51.8994	62.6645
65.1936	71.0813	73.6002
81.3943	90.5218	93.3068
95.8792	101.4699	105.8782
107.2259	116.6312	124.0561
134.4262	146.0761	150.1385
161.9787	166.8863	172.0600
185.9031	188.7494	201.6123
205.7022	218.5411	236.1824
243.3687	254.2569	297.1282
299.7446	308.6762	323.7695
328.1348	336.8311	339.6822
341.5936	359.3150	384.1354
398.8903	412.7890	420.3373
428.2372	436.4206	461.1922
467.2561	472.6616	475.7521
486.0711	489.4084	504.8159
509.4458	510.7993	517.2259
524.3828	528.0234	531.6558
540.8711	551.1254	560.7543
565.3480	574.9054	592.2354
595.4075	606.0386	611.6816
620.0627	639.4042	660.3645
686.1783	707.0705	731.1910
738.6568	758.3439	777.5657
778.0886	787.0950	787.8940
825.6086	847.8664	862.9828
891.5678	903.2211	905.6982
919.0942	926.9709	943.0251
944.9633	963.1298	971.9910
972.3031	1018.8748	1019.7790
1057.7968	1064.1662	1066.2742
1072.7853	1074.1358	1077.6797
1081.3925	1100.1681	1103.9078
1129.8068	1130.0144	1196.2647
1202.2353	1202.5736	1223.0412
1228.9283	1241.2681	1274.6433
1289.1533	1290.3896	1291.8274
1293.1591	1336.7742	1342.2484
1343.2508	1390.2526	1400.5758
1417.6121	1443.6708	1445.2105
1446.1603	1448.1516	1449.2471
1476.4473	1479.4379	1506.7564
1510.0028	1510.7128	1514.3960
1515.4345	1521.3721	1523.2959
1530.8275	1531.4192	1534.5132
1536.4669	1539.6384	1585.3225
1646.0551	1647.0712	1651.1798
1653.3527	1672.5996	1897.3579
1937.6625	2077.8113	2086.9772
2136.6502	3046.8504	3047.7188
3049.2066	3065.5320	3116.2548
3118.2276	3119.9466	3129.6720
3138.6553	3155.4196	3161.4496
3183.9574	3184.5369	3191.4043
3193.0401	3196.0464	3199.4826
3205.1388	3206.9867	3209.4711
3210.3947	3214.5555	3227.8886

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iii S=1

-8.9350	18.8664	24.3547
32.6931	38.1400	46.0139
47.5540	50.1817	56.6246
63.3100	65.9388	75.5850
78.4019	84.9926	88.1242
94.6753	107.1836	112.4276
117.7107	120.4553	123.8477
136.3279	142.2820	144.6262
148.1714	153.9193	158.6681
160.4021	167.1237	173.4105
175.4467	183.8170	186.2007
190.2816	195.6214	202.4845
217.7515	220.9238	225.4809
227.7333	234.6465	235.3314
247.5112	251.7340	267.3316
274.1069	284.4827	305.5196
314.8060	322.2928	328.3444

```
 332.8137   336.4093   340.8684
 348.3051   357.3404   364.1100
 374.7448   379.5538   381.6038
 393.1278   417.2884   426.1334
 446.3110   457.3726   463.4484
 472.7445   507.3035   509.2164
 512.2128   513.8392   515.5878
 517.6631   518.8663   521.2931
 525.0545   528.9038   532.9074
 542.6225   547.3131   561.5859
 563.7770   565.4945   574.0830
 581.0417   593.3817   599.4705
 618.6049   627.2912   638.2630
 641.1824   642.8884   651.0923
 708.9700   715.7443   717.9588
 732.9053   734.5567   745.7378
 755.8278   757.2928   765.9191
 773.9675   789.1644   791.3405
 792.8985   793.8071   796.1425
 818.1743   818.9375   823.8100
 868.5228   873.4760   892.9879
 897.9591   906.0658   910.0678
 911.3465   911.8740   914.8949
 924.2427   935.9933   940.5649
 942.5505   947.0525   949.7373
 964.0894   974.9867   975.6306
 976.0548   976.8087   983.0336
 985.1445   985.7190  1015.6417
1017.0643  1017.5267  1018.7956
1019.7385  1027.2068  1034.9712
1036.8848  1060.6100  1062.7105
1064.3309  1066.8162  1070.1192
1071.4630  1073.9329  1075.0908
1077.4867  1077.7950  1078.2778
1081.2336  1081.9123  1101.3556
1116.4052  1130.1934  1130.9040
1131.6538  1132.7698  1162.2823
1194.6148  1203.4212  1204.1576
1205.6784  1205.8315  1212.9488
1219.6348  1223.0422  1230.9840
1235.6901  1260.3006  1280.4648
1282.2800  1287.1152  1287.7729
1289.8354  1292.5148  1292.9638
1293.7168  1294.8117  1313.6522
1325.7069  1336.9522  1337.4826
1340.4114  1342.1386  1349.4972
1379.3127  1390.4412  1399.5743
1411.7926  1415.5753  1441.9650
1443.5576  1444.2356  1444.7925
1445.9083  1447.6143  1448.9288
1449.5282  1450.6151  1460.0756
1465.8688  1473.8893  1476.2678
1479.2637  1503.8786  1506.9601
1508.0460  1509.3876  1510.9982
1511.8423  1512.3135  1513.8088
1514.6144  1517.2327  1519.0910
1520.3001  1523.1364  1523.5149
1526.8372  1530.0655  1530.7650
1531.6354  1532.7220  1532.9704
1535.0379  1547.3003  1579.4975
1607.5117  1615.1315  1629.7312
1634.6346  1637.4889  1639.9909
1640.9810  1641.3072  1644.1385
1650.0731  1652.8057  1656.0766
1669.6241  1701.3630  3054.0181
3054.5842  3054.9581  3055.1842
3055.5212  3056.3916  3063.8272
3070.8207  3110.7006  3113.3026
3113.5616  3120.9894  3121.5151
3124.4569  3126.7743  3130.1991
3131.9428  3135.1208  3138.2527
3140.0677  3141.1647  3151.8457
3152.9635  3166.9254  3169.8554
3170.1574  3171.2888  3186.8767
3187.4655  3187.5926  3192.8932
3193.0740  3193.9848  3197.9844
3199.3366  3200.4897  3209.3881
3213.3871  3213.7425  3213.7995
3215.8374  3217.4748  3220.4532
3233.3524  3234.1231  3250.1779

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iii S=0
-----
  -7.6954    20.6649    25.8132
  35.1758    39.2491    48.2105
  53.7542    57.5954    64.3516
  65.8178    68.8380    76.1615
  84.9233    91.8112   106.0931
 107.3920   121.3407   128.3222
 135.8937   141.2460   149.6515
 154.7579   163.1313   167.7507
 170.7775   174.8528   176.4481
 177.9658   184.7220   186.8474
 188.2624   191.3379   201.2780
 207.1030   209.0770   216.1824
 217.6180   222.8563   227.7928
 232.6402   243.7033   245.1935
 254.3641   269.5646   288.5034
 291.9989   306.9674   312.5228
 320.3850   336.8027   342.1866
 344.1128   348.3015   354.4530
 364.6800   377.1377   383.2802
 406.6044   421.0890   427.3702
 434.0070   438.1933   455.8353
 462.4662   464.8602   469.5491
 496.1054   507.2562   512.2598
 513.8067   517.0734   521.3376
 522.4292   524.4492   525.0058
 527.8277   530.4895   532.7761
 549.4453   555.0004   569.3807
 578.4986   580.0524   583.8127
 599.0599   606.0353   610.7851
 612.7254   630.6232   637.4966
 641.9843   649.4999   657.8841
 702.2907   714.4712   728.1764
 732.3370   739.3186   746.4724
 752.5564   758.9263   768.2028
 777.6580   785.0996   791.3153
 795.4144   796.4254   800.4169
 819.4618   821.4492   824.3719
 873.8834   880.0424   887.5181
 892.4605   893.3333   910.5248
 911.6802   913.6656   917.9585
 919.8081   929.7301   933.3300
 944.0985   947.0221   947.7314
 949.3390   973.7935   977.5063
 978.9057   981.7135   982.3396
 988.0983  1003.5578  1015.6604
1016.1156  1017.4265  1020.2490
1022.0360  1026.0251  1034.6396
1048.0221  1057.1293  1059.7290
1062.4247  1068.7602  1071.8897
1073.4343  1074.2484  1074.8454
1077.3031  1077.5040  1077.9433
1078.3968  1091.4952  1094.3550
1115.5734  1128.1800  1132.7311
1133.9409  1136.3563  1181.3652
1193.3465  1204.3978  1204.5124
1205.2897  1206.7687  1215.1136
1215.3967  1219.1158  1231.2861
1240.8199  1259.6707  1281.3375
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1283.3557	1284.4669	1288.9885
1291.6503	1292.9356	1293.0822
1294.0616	1294.7294	1311.5443
1316.5843	1334.9519	1337.8458
1338.4380	1342.3199	1346.3045
1377.4588	1383.0900	1400.4849
1410.5059	1415.4565	1424.4555
1440.0903	1440.5583	1443.4366
1445.1767	1446.0863	1447.3039
1448.5165	1451.8765	1463.2098
1465.3196	1472.9647	1476.0968
1480.6699	1503.6292	1507.8127
1508.9563	1510.2229	1511.6901
1512.9517	1514.2657	1515.9524
1516.9688	1517.6016	1518.2024
1519.7340	1522.9774	1525.6014
1527.3689	1528.9817	1531.8667
1532.3280	1534.6394	1535.9499
1536.5138	1545.1589	1559.3638
1579.6439	1608.6311	1631.9154
1635.5368	1638.9279	1639.8965
1644.3830	1645.0050	1647.5417
1650.1735	1650.8773	1658.6955
1666.7129	1711.5293	3048.5861
3051.9204	3054.2922	3055.4048
3059.9726	3067.3118	3070.8889
3081.6924	3104.9392	3109.2126
3120.2375	3121.5760	3125.3403
3125.9403	3128.8995	3131.1480
3139.7545	3141.4515	3146.4325
3154.9650	3155.4666	3158.7498
3180.8832	3184.4422	3186.3428
3187.4238	3188.4811	3189.1479
3190.8910	3195.0868	3195.3626
3195.4906	3196.5029	3198.8043
3200.4794	3213.9795	3214.4166
3214.6194	3215.0958	3217.8442
3218.2633	3220.7894	3232.4558
3232.6199	3235.5103	3246.4320

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iv S=0

-8.2143	7.8886	18.4529
28.4829	29.1239	39.7168
46.2490	55.5719	64.7793
67.0926	77.7068	87.0585
115.7231	140.1478	156.6443
177.5982	184.8118	197.2840
210.2033	225.0521	229.7153
246.5349	250.6628	270.9966
311.8627	336.1176	342.7681
377.4563	385.9497	388.6973
411.9665	422.5925	423.0579
426.3435	443.7895	451.6884
454.6486	488.1220	517.3321
527.5474	560.7442	584.4299
604.5418	610.3326	620.0232
636.1238	636.7836	680.2983
690.8885	697.5935	713.3499
714.9660	777.8109	787.3103
787.5238	815.5378	850.3796
853.8310	863.3305	876.2759
894.0815	919.5176	929.4067
932.9501	943.4639	950.6259
970.4866	971.5475	972.2686
979.1914	1002.1073	1002.2411
1020.7659	1021.4408	1056.5931
1056.9101	1059.6687	1064.3542
1067.0383	1067.5608	1068.2232
1091.8266	1102.1564	1110.4042
1112.2181	1187.4802	1195.0970
1195.6317	1204.2878	1205.7184
1229.8512	1246.6004	1251.0726
1280.8626	1319.6147	1339.7839
1341.7423	1362.5127	1364.1749
1387.3236	1404.3935	1419.3579
1429.7028	1433.6016	1435.5957
1487.8638	1488.8396	1489.6161
1490.0524	1498.3820	1499.7644
1514.2818	1538.1671	1541.5710
1560.3594	1582.5105	1640.9782
1641.1310	1650.9074	1656.6760
1663.7046	2394.9206	2410.6493
3066.6260	3071.4607	3144.3618
3148.1148	3149.8114	3149.8629
3193.0950	3194.6114	3197.4498
3199.3980	3202.2146	3202.7071
3209.2211	3209.8929	3214.8830
3216.4391	3218.8652	3222.8812
3223.0520	3224.8781	3235.3568

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v S=0

7.5851	13.0702	25.6837
33.4680	34.5494	39.2830
41.1133	51.6313	62.5942
70.0900	75.4225	81.6503
96.4620	106.1073	111.3075
124.1828	132.3170	133.6959
147.9890	150.6843	159.0864
177.4506	185.2218	195.5174
198.5050	221.6668	231.7857
233.4350	235.2580	244.0635
265.6348	297.5121	304.2501
311.9237	321.1392	334.4717
346.4993	378.4001	386.1520
387.6624	407.9971	411.8960
425.3476	435.5277	450.8637
465.6994	470.4383	488.1845
506.5945	510.0376	522.5081
523.9310	530.8926	559.7716
576.4919	578.6841	598.8311
607.6299	610.0413	637.8964
660.9911	695.9154	729.0548
738.3306	761.2364	779.4291
785.5026	794.0137	794.2668
820.2598	865.9477	880.5632
891.6133	911.1975	912.6194
925.7955	930.1844	942.4856
945.4415	950.4734	971.6117
977.4149	980.2842	982.3576
1018.7128	1020.9635	1058.2777
1064.5507	1065.9062	1066.0607
1068.1098	1069.0776	1069.7726
1071.3218	1073.3169	1075.9114
1077.2468	1085.8288	1100.5478
1128.0640	1130.6394	1184.9309
1203.6025	1204.9693	1221.3110
1227.7964	1234.5116	1277.9618
1288.0096	1290.1359	1293.9713
1294.9512	1318.1239	1341.4219
1341.7403	1381.7742	1400.4620
1413.4368	1428.6822	1431.6017
1433.0441	1440.3025	1442.1784
1444.9548	1447.3995	1475.6284
1480.3375	1487.4368	1488.4871
1488.8559	1489.2787	1504.9242
1509.0691	1510.9240	1512.1937
1516.8052	1521.1898	1525.5741
1530.7408	1532.5879	1534.0954

1535.5256 1567.8043 1582.0260
1644.1364 1645.2575 1649.5794
1651.6553 1658.7636 2391.2338
2411.2114 3051.4171 3055.3763
3056.9598 3057.6559 3066.3201
3070.3007 3107.3628 3111.0451
3114.8683 3119.5381 3141.8456
3144.7423 3147.1327 3148.1052
3149.2940 3150.3265 3155.1499
3161.8947 3187.2378 3189.0824
3195.2656 3195.3055 3198.9753
3199.5937 3214.3900 3215.5011
3216.1503 3222.5107 3235.3096

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unbridged Co2(CO)8

  22.8490   24.4557   54.0847
  58.2247   59.1891   73.2400
  73.8847   82.2795   82.4373
  94.4677   94.5925   102.5125
 102.6188   103.3758   105.4345
 170.6639   314.2522   324.7259
 326.8377   326.9815   335.4918
 335.6166   403.5475   428.6094
 428.6526   437.8580   466.5484
 467.2250   470.3213   496.3478
 499.2270   499.5802   508.5809
 508.9239   551.3650   551.3803
 551.4581   551.5003   554.0748
 572.6726 2092.0770 2092.3461
2099.3683 2110.6941 2110.7414
2127.8491 2150.3726 2195.3547

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bridged Co2(CO)8

  23.6912   38.4660   38.8260
  63.2649   68.2206   75.6973
  76.1940   86.8009   88.2932
  92.4025   94.8356   109.1090
 111.4334   223.2486   235.1909
 255.1524   315.2740   315.6078
 329.7798   353.5114   356.9798
 361.7722   417.6901   431.4739
 435.2898   436.4138   446.3864
 449.7584   464.4920   477.6771
 478.3903   479.9080   516.5748
 521.8719   525.9032   538.7023
 565.3561   577.8573   604.1686
 701.8616 1943.6026 1958.1314
2120.8279 2121.5715 2128.6342
2131.5245 2153.1688 2195.5688

Table S10. Energies (E_h) for all optimized structures.

Species	E(SCF)	H(gas)	G(gas)
i	-4229.517222	-4229.143570	-4229.240930
iib	-4386.810610	-4386.319646	-4386.427241
iii$_{S=1}$	-3491.957048	-3491.089139	-3491.220039
iii$_{S=0}$	-3491.954578	-3491.085076	-3491.210498
iv	-2545.494020	-2545.073675	-2545.163084
v	-2702.793091	-2702.253493	-2702.359224
unbridged $Co_2(CO)_8$	-3672.090550	-3672.001451	-3672.078294
bridged $Co_2(CO)_8$	-3672.098101	-3672.008981	-3672.083200

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